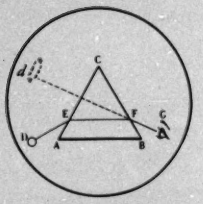


optics and spectroscopy

volume vii
number 5
november 1959

OPTICAL SOCIETY OF AMERICA

RUSSIAN EDITORIAL STAFF

Editor: S. E. FRISH

Assistant Editor: P. P. FEOFILOV
Corresponding Secretary: L. S. SAZONOV

Associate Editors:

M. M. GUREVICH M. A. EL'IASHEVICH A. A. LEBEDEV V. P. LINNIK
S. L. MANDEL'SHTAM I. V. OBREIMOV V. K. PROKOF'EV
N. N. SOBOLEV A. N. TERENIN A. I. TUDOROVSKII

Translated on the Initiative of
THE OPTICAL SOCIETY OF AMERICA, INC.
With a Grant-in-Aid from
THE NATIONAL SCIENCE FOUNDATION

TRANSLATION EDITORIAL STAFF

Scientific Editors

FRED W. BEHNKE, *Perkin-Elmer Corp.*

CYRUS FELDMAN, *Oak Ridge National Laboratory*

GEORGE HERRMAN, *Columbia University*

Administrative Editor: PATRICIA R. WAKELING, *OSA*

Published monthly by the Optical Society of America, Inc. Executive office: 1155 Sixteenth Street, N.W., Washington, D.C. Subscriptions for one year to members of the Society: Associates $13.00; Regular members and Fellows $17.00. Subscriptions for non-members of the Society: One year U. S. and Possessions, $25.00; Foreign $28.00. Back numbers: $3.00 per copy. Subscriptions, changes of address and undeliverable copies should be referred to the Executive offices in Washington, D.C. The office of publication is 2500 South State Street, Ann Arbor, Michigan. Second class postage paid at Ann Arbor, Michigan.

Printed in the U.S.A. by Edwards Brothers, Inc., Ann Arbor, Michigan.

CALCULATION OF SOME PARAMETERS OF MONOSUBSTITUTED BENZENE MOLECULES BY THE "METAL" MODEL METHOD

A. F. Terpugova

Received 3 March 1959

The energy levels and wave functions of $C_6H_5NH_2$, C_6H_5Cl, C_6H_5Br, C_6H_5F, C_6H_5N, $C_6H_5NO_2$ molecules are calculated by the "metal" model method. The spectra of these compounds in the visible and ultraviolet regions are interpreted by means of comparison with the spectrum of benzene. Calculation of the wave functions of the indicated molecules allows one to draw conclusions about their electron density distributions and about the orientational action of the substituent.

INTRODUCTION

There has always been more than one point of view on the subject of interpretation of absorption bands in the spectra of monosubstituted benzenes. The spectra of these compounds have two regions of absorption: 2600-3000 A and 2200-2400 A.

The absorption band 2600-3000 A has been interpreted by all authors as a displaced and permitted benzene band, corresponding to the forbidden transition of the benzene molecule from λ = 2600 A.[1, 2] Some authors[3] consider the absorption band in the region 2200-2400 A as a displaced and permitted band of benzene from λ = 1980 A; others believe that this transition cannot be interpreted as pertaining to benzene, since the difference in the position of the maxima of the absorption bands is sometimes as high as 800 A, and aside from this, in the absence of the first band, this band does not have the benezene vibrational structure.

Nakagura and Tanaka[4] propose that the second band be considered the result of the transition between levels W_n and W_s, which do not pertain to benzene, but arise in consequence of interaction between the entirely filled benzene level H_b and the vacant level v_s of the substituent.

In considering the question of the interpretation of the spectra of monosubstituted benzene molecules, one must take into account the presence in these compounds of triplets of metastable levels, the existence of which is confirmed by a number of photochemical studies.[5]

1. CALCULATION OF THE ENERGY LEVELS OF THE COMPOUNDS C_6H_5Cl, C_6H_5Br, C_6H_5F, AND $C_6H_5NH_2$

The structure of the molecule is that of a ring with a branch. In comparison with benzene, the molecule of which is ring shaped, the above molecules have a branch or an extra "intersection."

Six π-electrons of the benzene ring and indivisible pairs of p-electrons of the substituent move freely in a potential depression with an infinitely high barrier at its end (the depression has the form of a ring with a branch). The influence of a substituent of the first type is manifested by the displacement of the π-electrons toward the substituent. This displacement is considered an auxiliary potential depression, which is situated at the position of the substituent atom.

The depth of the depression is taken as $\Delta U = I_X - I_C$, where I_X is the first ionization potential of the substituent atom, and I_C is the first ionization potential of the carbon atom. The width of the depression is taken equal to the dimensions of substituent atom (Fig. 1).

All calculations were carried in a system of atomic units. For electrons in the potential depression, Schrödinger's equation is written

$$\frac{d^2\psi}{ds^2} = 2(E - U)\psi,$$

where

$$U = -\nu \text{ for } 0 \leqslant s_1 \leqslant L_1;$$

$$U = 0 \text{ for } 0 \leqslant s_2 \leqslant L_2,\ 0 \leqslant s_3 \leqslant L_3$$

(L_1 is the diameter of the substituent atom, L_2 is the difference in lengths of the C-X band and the radius of the X atom.)

The solution of this equation is written in the form

$$\psi_1 = A_1 \sin \beta s_1 \qquad \text{for } s_1 \text{ from 0 to } L_1,$$

$$\psi_2 = A_2 \sin \alpha s_2 + B_2 \cos \alpha s_2 \qquad \text{for } s_2 \text{ from 0 to } L_2,$$

$$\psi_3 = A_3 \sin \alpha s_3 + B_3 \cos \alpha s_3 \qquad \text{for } s_3 \text{ from 0 to } L_3$$

(L_2 is equal to 6σ, where σ is the length of a C····C band in the benzene ring).

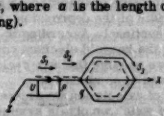


Fig. 1. Model of the molecule $C_6H_5NH_2$.

Writing the conditions of combination of these similar wave functions at the points p and q (Fig. 1) and the conditions of combination of the derivatives in the form

$$\sum_i \frac{\partial \psi_i}{\partial x_i} = 0,$$

and also using the properties of symmetry of the molecule, we obtain equations for α.

In the given case we have used the conditions of continuity of similar wave functions at the points p and q. In reference 6 Borovinsky assumes that these conditions were not true. However, detailed examination of this problem in reference 7 shows that the assertion of Borovinsky is questionable. Our calculations are made under the assumption of the truth of the conditions of continuity of the wave functions at the points of combination.

Bearing in mind the properties of the symmetry of the molecule, we obtain two sorts of condition: symmetric and antisymmetric relative to the plane XZ (Fig. 1).

For the symmetric condition we derive the equation

$$2\left(\frac{\beta}{\alpha}\cos\beta L_1 \cdot \sin\alpha L_2 + \sin\beta L_1 \cos\alpha L_2\right) + \left(\frac{\beta}{\alpha}\cos\beta L_1 \cos\alpha L_2 - \sin\beta L_1 \sin\alpha L_2\right)\cot\frac{\alpha L_2}{2} = 0,$$

and for the antisymmetric

$$\sin\alpha L_2 = 0.$$

Table 1. Position of the First Absorption Band

Compound	Calculated	Experimental
C_5H_5N	3800	3400–2400 [8]
C_6H_5Cl	2807	2750–2430 [9]
C_6H_5Br	2850	2780–2400
C_6H_5F	3070	2644–2400

The absorption band of greatest wavelength is obtained at the transition from the last entirely filled level to the first unfilled one.

Table 1 shows the data we have calculated for the first absorption band of the molecules. Experimental data are given for comparison.

2. CALCULATION OF THE MOLECULE C_5H_5N

Calculation of the energy levels and of the transitions of greatest wavelength for the pyridine molecule is performed in the same manner as in section 1. The molecule is ring shaped with an auxiliary potential depression at the location of the nitrogen atom (Fig. 2). The depth and width of the depression are chosen in the same way as in section 1. According to chemical data, pyridine retains the benzoid electron configuration, and because of this we assume that six π-electrons participate in the process of combination.

As a result of calculation we arrive at two equations, in the solution of which we obtain symmetric and antisymmetric conditions relative to the plane XZ (Fig. 2).

Fig. 2. Model of the C_5H_5N molecule.

For the symmetric condition the equation has the form

$$\frac{\alpha}{\beta}\tan\frac{\alpha L_1}{2} + \tan\frac{\beta L_2}{2} = 0,$$

and for the antisymmetric condition

$$\frac{\alpha}{\beta}\cot\frac{\alpha L_1}{2} + \cot\frac{\beta L_2}{2} = 0.$$

Solving these equations, we find α, and consequently, also E.

For the first two transitions of longest wavelength for pyridine we obtain the values $\lambda = 2094$ A and $\lambda = 1993$ A.

3. CALCULATION OF THE ENERGY LEVELS AND LONGEST WAVELENGTH TRANSITIONS FOR THE $C_6H_5NO_2$ MOLECULE

The group $-NO_2$, in distinction from the groups $-Cl$, $-Br$, $-F$, $-NH_2$, is an orientor of the second type. In the $C_6H_5NO_2$ molecule the induction effect displaces electrons from the substituent toward the benzene ring. The direction of displacement of the electrons caused by the induction effect and that caused by the combination effect coincide in this case. We assume that it is unnecessary to adduce an auxiliary potential depression in the calculation of such molecules. Actually, bearing in mind the direction of the inductive effect, we would have to establish an auxiliary depression at the location of the benzene ring, but inasmuch as the electrons in the branch move less freely than those in the ring (they do not mingle with the π-electrons of benzene, but are only displaced toward them), we assume that it is inappropriate to adduce the auxiliary depression in the benzene ring.

We propose to classify the models of the molecules of monosubstituted benzene with substituents of the first and second types, in the framework of the "metal" molecule method, according to the presence or absence of an auxiliary potential depression at the location of the substituent atom. The auxiliary potential depression is adduced in the case of the presence of a substituent-orientor of the first type, but not of the second.

The choice of a coordinate system for the model of the nitrobenzene molecule is shown in Fig. 3.

Fig. 3. Model of the $C_6H_5NO_2$ molecule.

The solution was carried out by the same method as in section 1.

For the symmetric condition relative to plane XZ (Fig. 3), the equation obtained was

$$2(2\cos\alpha L_1 \cdot \sin\alpha L_2 + \sin\alpha L_1 \cdot \cos\alpha L_2) - (2\cos\alpha L_1 \cdot \cos\alpha L_2 - \sin\alpha L_1 \sin\alpha L_2)\cdot\cot\alpha\frac{L_2}{2} = 0.$$

For the antisymmetric condition relative to the same plane, the equation has the form

$$\sin\alpha L_2 \cdot \sin\alpha L_1 = 0.$$

From these solutions the energy levels of the molecules and the frequencies of the longest wavelength transitions have been found. The results of the calculations are shown in Table 2, in which the second column gives the experimental data on the positions of the absorption bands of nitrobenzene in nonpolar solution.[8, 9]

Table 2. Position of the Long Wavelength Absorption Bands for the Molecule $C_6H_5NO_2$

Calculated	Experimental
1910	2000
2089	2150
2554	2600
2756	2900
4275–4867	3500–5000

4. CALCULATION OF ELECTRON DENSITY

The wave functions which have been found for all states of E_i allow us to compute, for all the molecules under consideration, the quantity $|\Psi|^2 = \sum |\psi_i|^2$ (ψ_i is the wave function of the energy state E_i).

The quantity $|\Psi|^2$ is proportional to the density of electrons in these molecules. Inasmuch as the orienting action of the substitute is determined by the density distribution of the indicated electrons, we can judge by the form of the function $|\Psi|^2$ how accurately this action is represented by the "metal" model.

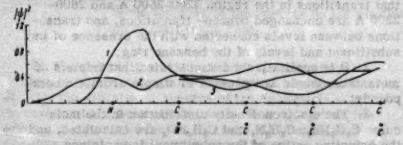


Fig. 4. Curves of $|\Psi|^2$ for monosubstituted benzenes. Curve 1—$C_6H_5NH_2$; curve 2—$C_6H_5NO_2$; curve 3—C_5H_5N.

Curves 1, 2, and 3 in Fig. 4 show the shape of the function $|\Psi(s)|^2$ (s is a running coordinate) for aniline, nitrobenzene, and pyridine. Curve 1 shows that the maximal electron density corresponds to the ortho- and para-positions; there is a minimum of electron density for the meta-position.

If there is in the ring a second electrophilic substituent, it will, according to experimental data, occupy with highest probability the ortho- and para-positions. Our attention is attracted to the fact that for the molecule of nitrobenzene the magnitude of electronic density, in many portions of the molecule, is several times smaller than for the aniline molecule. This agrees well with experimental data that a substituent of the first type activates, and one of the second kind passifies, the benzene ring in relation to subsequent substitutions. However, in the $C_6H_5NO_2$ molecule the electron density is, as before, greater in the ortho- and para-positions than in the meta-position. Thus, in this case, calculation does not clarify the nature of the orienting action of the $-NO_2$ group.

It is seen in curve 3 that in pyridine the electron density is minimal in the ortho-position and maximal in the para- and meta-positions. The latter is verified by chemical data: electrophilic substituent occupies with highest probability the ortho-position of the pyridine molecule.

Comparing our results with the results of calculation by the LCAO method,[10] we see that, for the pyridine and aniline molecules, both methods yield a correct explanation of the orienting action of the substituent. For the nitrobenzene molecule, the results of the LCAO calculation gives a value for electron density in the meta-position which is almost equal to the value of the electron density in the ortho-position, and a slightly smaller value in the para-position.

5. CONSIDERATION OF RESULTS

Having calculated the energy spectra of pyridine, aniline, and nitrobenzene, and knowing the spectrum of benzene,[11] one can attempt to interpret these spectra. We outline the scheme of terms of these molecules (Fig. 5).

Calculation of the benzene spectrum, without taking into account the mutual repulsion of the electrons or the interaction between the electron and wave motions, gives an energy spectrum in which all levels except the first are double. The longest wavelength transition is obtained by a quadruple degeneration from $\lambda = 1950$ A.

Our data for the monosubstituted benzene molecules was also obtained without consideration of the mutual repulsion of electrons or the interaction between electron and wave motions, so that it should be compared with appropriate data, and not with the data of the more recent works on the benzene spectrum.[12] After degeneration transition 1 (Fig. 5) gives three transitions, which are identified with the well-known transitions of the benzene spectrum 2800-2200 A, 2050-1850 A, and 1850-1650 A.[13]

The levels of pyridine are a little lower than those of benzene, and are dispersed. Instead of a single quadruply degenerate transition, we obtain in pyridine the two transitions 1 and 1′ with $\lambda = 1993$ A and $\lambda = 2094$ A, which can be identified with the bands 2947-2083 A and 2083-1930 A in the spectrum of pyridine. Therefore the electron spectrum of pyridine can be considered as a modification of that of benzene, inasmuch as the transition in pyridine takes place between the same levels as in benzene.

Considering the energy levels of aniline (all other derivatives of benzene with substituent-orientators of the first type have the same system of levels) it is easy to notice that the levels ε_1, ε_2, ε_3 are merely modifications of those of benzene (the level ε_3 is perfectly coincident with that of benzene). The level X in this molecule appears in consequence of the presence of the group $-NH_2$.

The existence of the $-NH_2$ group indicates the presence of a branch on the benzene ring. The ring-branch system has other levels in addition to those peculiar to benzene (the first of these we have indicated by the letter X). The position of this level depends upon the characteristics of the substituent, i.e., upon the depth and width of the auxiliary potential depression which is located at the position of the substituent atom. For the indicated substituent this level is at approximately the same distance from level ε_3 as coincides exactly with the benzene level. The bands in the aniline spectrum with $\lambda = 3800$ A and $\lambda = 2514$ A, which can be identified with the experimentally observed bands 3200-2400 A and 2400-2030 A,[11] arise in consequence of the transition from the level X to the distributed levels of the benzene ring.

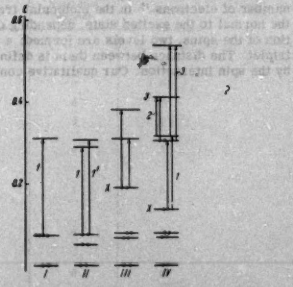


Fig. 5. Energy spectra of the molecules C_6H_6 (I), C_5H_5N (II), $C_6H_5NH_2$ (III), and $C_6H_5NO_2$ (IV).

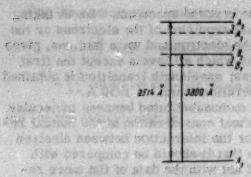


Fig. 6. General composition of the molecule $C_6H_5NH_2$.

In the nitrobenzene molecule there is in addition to the level X a level Y also, connected with the presence of a second branch (the N⟶O band). The nitrobenzene spectrum is taken as consisting of the following groups of transitions: (1) transitions analogous to the aniline transitions from level X to the benzene levels (λ = 2556 A and λ = 2756 A) which we identify with bands λ = 2600 A and λ = 2900 A; (2) transitions from the benzene levels ε_2, ε_3 to level Y (λ = 4275 A and λ = 4867 A). These transitions we identify with the broad band in the nitrobenzene spectrum which has a maximum at 3500 A, and continues through the visible region to 5000 A; (3) transitions between levels of the benzene ring (λ = 2099 A and λ = 1980 A), which we identify with the bands λ = 2000 A and λ = 2150 A.

Thus, in the system of the ring with the branch, other levels appear in addition to those of benzene because of the existence of the branches.[14] This is natural since our system consists of two subsystems, each of which has its own energy spectrum. In uniting them into one system we receive levels belonging to both subsystems. The electron spectra of similar compounds are obtained from transitions from levels connected with the presence of the substituent itself to the levels of the benzene ring, and from the levels of the benzene ring to levels which exist because of the branch. Thus the nature of the electronic spectra of these compounds is distinct from the nature of the benzene transitions.

If we write the general composition of the molecule, as is done in reference 14, we will obtain the following scheme (Fig. 6) for monosubstituted benzenes, where A are levels symmetric with respect to the plane XZ, and B are levels antisymmetric with respect to the same plane.

In the aromatic compounds there is always an even number of electrons.[15] In the molecular transitions from the normal to the excited state, depending on the orientation of the spins, two levels are formed: a singlet and a triplet. The distance between them is defined exclusively by the spin interaction. Our qualitative concept agrees well with the view of Terenin concerning the presence of triplet metastable levels in simple aromatic compounds. In order to obtain these levels automatically from the calculation, it is necessary to take account of the interaction of π-electrons in the system (this is done for the benzene molecule in reference 10).

CONCLUSIONS

1. An interpretation of the electron spectra of molecules of monosubstituted benzenes is given. It is shown that transitions in the region 3200-2600 A and 2600-2200 A are unchanged benzene transitions, and transitions between levels connected with the presence of the substituent and levels of the benzene ring.

2. It is qualitatively demonstrated that triplets of metastable levels are present in simple aromatic compounds.

3. The electron density distribution in the molecules $C_6H_5NH_2$, C_6H_5N, and $C_6H_5NO_2$ are calculated, and the orienting action of the substituent is explained.

In further work doubly-substituted benzenes with the same or differing substituents are calculated.

In conclusion, I express sincere gratitude to N. A. Prilezhaeva for her constant help in the work, and also to V. I. Danilova for valuable advice and guidance.

REFERENCES

1. H. Sponer. Rev. Mod. Phys. **22**, 224 (1942).
2. A. L. Sklar. Rev. Mod. Phys. **14**, 232 (1942).
3. A. Walsh. Trans. Farad. Soc. **42**, 62 (1946).
4. I. Nagakura and J. Tanaka. J. Chem. Phys. **22**, 236 (1954).
5. A. N. Terenin. "Fotokhimiya Krasitelei." (Dye Photochemistry), Leningrad, 1947.
6. L. A. Borovinsky. Opt. i Spektr. **4**, 526 (1958).
7. T. K. Rebane. Opt. i Spektr. **6**, 266 (1953).
8. A. Wenzel. J. Chem. Phys. **22**, 1623 (1954).
9. N. S. Bayliss and E. J. McRal. J. Phys. Chem. **58**, 1066 (1954).
10. K. Fukin, T. Yonezawa, C. Nagata, and H. Shingu. J. Chem. Phys. **22**, 1433 (1954).
11. M. V. Volkenshtein. "Stroenie i Fizicheskie Svoistva Molekul." (Structure and Physical Properties of Molecules), Moscow-Leningrad, 1955.
12. L. A. Borovinsky. Opt. i Spektr. **4**, 156 (1958).
13. Landolt-Bornstein. "Zahlenwerten und Funktionen." 1955.
14. W. Bingel. Z. Naturforsch. **10a**, 462 (1955).
15. O. A. Reutov. "Teoreticheskie Problemi Organicheskoi Khimii." (Theoretical Problems of Organic Chemistry), Moscow, 1956.

CALCULATION AND INTERPRETATION OF VIBRATIONAL SPECTRA OF NAPHTHENES
III. CYCLOPENTANE AND DEUTEROCYCLOPENTANE

L. M. Sverdlov and N. I. Prokof'eva

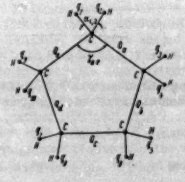
Received 31 January 1959

Calculations are made of the frequencies of normal vibrations using the model D_{5h}, and a complete interpretation is given of the infrared absorption and Raman spectra of cyclopentane and deuterocyclopentane.

Some features of the spectra do not preclude the possibility of a small out-of-plane distortion of the carbon ring.

1. The calculation of vibrational spectra of cyclopentane is of a particular interest for several reasons. Firstly, the vibrational spectra of the cyclopentane hydrocarbons have been studied more thoroughly than the spectra of other naphthenes, because all investigated naphthas contain cyclopentane which forms an essential part of the benzene fractions. Furthermore, the knowledge of the force constants of cyclopentane will permit the calculation of the vibration spectra of alkylcyclopentanes of various types, and the determination of the characteristic frequencies of the corresponding homologous series; this should prove very helpful in the molecular spectral analysis of complex mixtures. Secondly, the structure of cyclopentane is very important for the theory of chemical structure. It is still being debated whether the cyclopentane ring is planar (i.e., C_5H_{10} belongs to the symmetry type D_{5h}), or whether it is nonplanar (i.e., C_5H_{10} has a lower cymmetry C_{2v}, C_s, C_1). The opinions of the spectroscopists are divided in this respect: the majority adheres to the nonplanar model[1-4]; some adhere to the other point of view.[5]

In order to decide between these two models it is obviously necessary to make a rigorous calculation of the vibrational frequencies of cyclopentane and deuterocyclopentane on the basis of the planar model, using the method of M. A. El'iashevich and B. A. Stepanov, and to attempt a complete interpretation of the available experimental data.



2. The cyclopentane molecule has 39 normal vibrations. For the purposes of calculations, we introduce 55 internal vibrational coordinates—changes of the bond lengths and of the angles: q_i (i = 1-10); Q_a, Q_b, Q_c, Q_d, Q_e; γ_{ab}, γ_{bc}, γ_{cd}, γ_{de}, γ_{ea}; α_{12}, α_{34}, α_{56}, α_{78}, $\alpha_{9,10}$; $\beta_{a,i}$ (i = 1-4); $\beta_{b,i}$ (i = 3-6); $\beta_{c,i}$ (i = 5-8); $\beta_{d,i}$ (i = 7-10); $\beta_{e,i}$ (i = 9,10,1,2,) (see Figure); $\rho^a_{b,c}$, $\rho^a_{c,d}$, $\rho^b_{c,d}$, ρ^b_{ab}, ρ^c_{ab}, ρ^c_{ea}, ρ^d_{ea}, ρ^d_{cb}, ρ^e_{ab}, ρ^e_{bc}. Here $\rho^a_{b,c}$ is the displacement of the a-bond out-of-plane of the bonds b and c. There are 16 redundancy relations between the coordinates. Table 1 gives the number and the type of vibrations of the different symmetry types, and the selection rules for the point group D_{5h}. Next, it is necessary to calculate the symmetry coordinates for the group D_{5h}. Unfortunately, there is no table of symmetry coordinates for this group

Table 1. Classification of Vibrations of Cyclopentane for the group D_{5h}

Symmetry type	Character of vibrations	Raman spectrum		Infrared spectrum	
		Total line number	$\nu < 1500$ cm^{-1}	Total line number	$\nu < 1500$ cm^{-1}
A'_1	ν_1 (Q), ν_2 (e), ν_3 (q)	3p	2p	0	0
A''_1	ν_4 (β)	0	0	0	0
A'_2	ν_5 (β)	0	0	0	0
A''_2	ν_6 (β), ν_7 (q)	0	0	2	1
E'_1	$\nu_{8,9}$ (Q), $\nu_{10,11}$ (β1a) $\nu_{12,13}$ (e), $\nu_{14,15}$ (q)	0	0	4	3
E''_1	$\nu_{16,17}$ (β1a), $\nu_{18,19}$ (β11b) $\nu_{20,21}$ (q)	3d	2d	0	0
E'_2	$\nu_{22,23}$ (τ) $\nu_{24,25}$ (Q) $\nu_{26,27}$ (β), $\nu_{28,29}$ (e), $\nu_{30,31}$ (q)	5d	4d	0	0
E''_2	$\nu_{32,33}$ (r), $\nu_{34,35}$ (β1a) $\nu_{36,37}$ (β1b), $\nu_{38,39}$ (q)	0	0	0	0

Denotations: p – polarized; d – depolarized.

in the monograph, reference 6. Therefore we have deduced explicitly the coefficient matrices of the irreducible representations of the group D_{3h}, and by the procedure of El'iashevich obtained the symmetry coefficients of the group D_{3h} given in Table 2. In order to obtain the symmetry coordinates, it is necessary to find the characteristic symmetry of the various coordinates and to multiply the coordinate columns by the coefficient columns. As an example, we give here some of the symmetry coordinates of the species E_2'':

$$p^{a_1''II_b} = \frac{1}{\sqrt{10}}\left((\beta_{n1} + \beta_{n2} + \beta_{n3} + \beta_{n4}) + \cos 144\,(\beta_{n3} + \beta_{n5} + \beta_{n9} + \beta_{n10} + \beta_{n4} + \beta_{n8} + \beta_{n3} + \beta_{n10} + \beta_{n4}) + \cos 72\,(\beta_{n5} + \beta_{n7} + \beta_{n6} + \beta_{n8} + \beta_{n6} + \beta_{n7} + \beta_{n8} + \beta_{n8})\right).$$

$$p^{a_1''II} = \frac{1}{\sqrt{5}}\left((\eta_1 + \eta_2) + \cos 144\,(\eta_3 + \eta_4 + \eta_9 + \eta_{10}) + \cos 72\,(\eta_5 + \eta_6 + \eta_7 + \eta_8)\right).$$

The following redundancy relations between the symmetry coordinates of different types exist:

1) $\gamma^{a_1''} = 0$; 2) $\cot\Phi \cdot \tan\frac{\theta_2}{2} \cdot \alpha^{a_1''} - \beta^{a_1''} = 0$; 3) $\rho^{a_1''} = 0$; 4) $\rho^{a_2''} = 0$;

5, 6) $\gamma^{a_1''I} + 2\sin 36 \cdot \sigma_c \cdot Q^{a_1''I} = 0$; 7, 8) $\cot\Phi \cdot \tan\frac{\theta_1}{2} \cdot \gamma^{a_1''I} + \cot\Phi \cdot \tan\frac{\theta_2}{2} \cdot \alpha^{a_1''I} - \beta^{a_1''I_b} = 0$;

9, 10) $\cot\Phi \cdot \tan\frac{\theta_1}{2} \cdot \gamma^{a_2''I} + \cot\Phi \cdot \tan\frac{\theta_2}{2} \cdot \alpha^{a_2''I} - \beta^{a_2''I_b} = 0$;

11, 12) $\rho^{a_2''I_a} = 0$; 13, 14) $\rho^{a_2''I_b} = 0$;

15, 16) $\rho^{a_1''I_b} + \rho^{a_2''I_a} \cdot \cot 144 = 0$.

Here $\theta_1 = \angle CCC$; $\theta_2 = \angle HCH$; $\Phi = \angle CCH$; $\sigma_c = r(C-H)/r(C-C)$. Next, after complicated calculations, the symmetrized matrices of the kinematic coefficients were obtained in the general and in the numerical form. The following geometrical parameters were used in this work[8]: r(C—H) - 1.09 A, r(C—C) = 1.54 A, $\theta_1 = 108°$, $\theta_2 = 109°28'$. The anharmonicity was taken into consideration by the "spectroscopic mass" method.[6]

For calculation of the potential energy matrix, the following force interactions were considered: the diagonal coefficients (K_q, K_Q, K_α, K_β, K_γ, K_ρ); the interactions of the neighboring C—H bonds between themselves (h) and with the bonds C—C (H); the interactions of the bonds C—H with the adjacent angles α, β, $\gamma(a_\beta, a_\alpha, b_\gamma, b_\beta)$; the interactions of the bonds C—C with the adjacent angles α, $\beta(A_\beta, B_\alpha)$; all interactions in the ring; the interactions of the angles α with the adjacent $\beta(\beta_{\alpha\beta})$ and $\gamma(\alpha_{\alpha\gamma})$ angles; and the interactions of the angles β with the adjacent angles $\beta(l, m, n)$, $\gamma(l, m, n)$ and ρ.

The symmetrized force coefficients that correspond to vibrations of the species A_2', A_2'', E_1', E_1'', E_2' form 40 linearly independent combinations, for the calculation of which the 34 frequencies can be used that are permitted

Table 2. Symmetry Coefficients for the Group D_{3h}

Symmetry operations	Characteristic symmetry			Types of symmetry coordinates																					
	C_{2y}	–	–	A_1'	–	–	–	–	–	$E_1'I$	$E_1'II$	–	–	–	–	–	–	$E_1''I$	$E_1''II$	–	–	–	–	–	–
	–	$C_2^{(z)}$	–	A_2''	–	–	–	A_2''	–	$E_1''I$	$E_1''II$	$E_1''I$	$E_1''II$	–	–	–	–	$E_1'I$	$E_1'II$	$E_1'I$	$E_1'II$	–	–	–	–
	–	–	σ_i	A_1'	A_1''	A_2'	A_2''	$E_1'Ia$	$E_1'IIa$	$E_1'Ib$	$E_1'IIb$	$E_1''Ia$	$E_1''IIa$	$E_1''Ib$	$E_1''IIb$	$E_1'Ia$	$E_1'IIa$	$E_1''Ib$	$E_1''IIb$	$E_1'Ia$	$E_1'IIa$	$E_1''Ib$	$E_1''IIb$	$E_2'Ia$	$E_2'IIa$	$E_2''Ib$	$E_2''IIb$
C_1	Q_1	η_1	β_{n1}	1	1	1	1	1	0	0	1	1	0	0	1	1	0	0	1	1	0	0	1		
C_3	Q_4	η_3	β_{n3}	1	1	1	1	a_1	$-b_1$	b_1	a_1	a_1	$-b_1$	b_1	a_1	a_2	$-b_2$	b_2	a_2	a_2	$-b_2$	b_2	a_2		
C_3^2	Q_5	η_4	β_{n9}	1	1	1	1	a_1	b_1	$-b_1$	a_1	a_1	b_1	$-b_1$	a_1	a_2	b_2	$-b_2$	a_2	a_2	b_2	$-b_2$	a_2		
C_3^2	Q_6	η_5	β_{n5}	1	1	1	1	a_2	$-b_2$	b_2	a_2	a_2	$-b_2$	b_2	a_2	a_1	b_1	$-b_1$	a_1	a_1	b_1	$-b_1$	a_1		
C_3^2	Q_8	η_7	β_{n7}	1	1	1	1	a_2	b_2	$-b_2$	a_2	a_2	b_2	$-b_2$	a_2	a_1	$-b_1$	b_1	a_1	a_1	$-b_1$	b_1	a_1		
σ_h	–	η_2	β_{n2}	1	-1	-1	1	0	0	1	-1	0	0	-1	1	0	0	1	-1	0	0	-1		
$C_2^{(1)}$	–	–	β_{n4}	1	1	-1	-1	-1	0	0	1	-1	0	0	1	-1	0	0	1	-1	0	0	1		
$C_2^{(2)}$	–	–	β_{n8}	1	1	-1	-1	$-a_2$	b_2	b_2	a_2	$-a_2$	b_2	b_2	a_2	$-a_1$	$-b_1$	$-b_1$	a_1	$-a_1$	$-b_1$	$-b_1$	a_1		
$C_2^{(3)}$	–	–	β_{n10}	1	1	-1	-1	$-a_1$	$-b_1$	$-b_1$	a_1	$-a_1$	$-b_1$	$-b_1$	a_1	$-a_2$	$-b_2$	$-b_2$	a_2	$-a_2$	$-b_2$	$-b_2$	a_2		
$C_2^{(4)}$	–	–	β_{n6}	1	1	-1	-1	$-a_1$	b_1	b_1	a_1	$-a_1$	b_1	b_1	a_1	$-a_2$	b_2	b_2	a_2	$-a_2$	b_2	b_2	a_2		
$C_2^{(5)}$	–	–	β_{n9}	1	1	-1	-1	$-a_2$	$-b_2$	$-b_2$	a_2	$-a_2$	$-b_2$	$-b_2$	a_2	$-a_1$	b_1	b_1	a_1	$-a_1$	b_1	b_1	a_1		
$\sigma_v^{(1)}$	–	–	β_{n1}	1	-1	-1	1	0	0	1	1	0	0	-1	-1	0	0	1	1	0	0	-1		
$\sigma_v^{(2)}$	–	–	β_{n3}	1	-1	-1	1	$-a_2$	b_2	b_2	a_2	a_2	$-b_2$	$-b_2$	$-a_2$	$-a_1$	b_1	b_1	$-a_1$	a_1	b_1	b_1	$-a_1$		
$\sigma_v^{(3)}$	–	–	β_{n5}	1	-1	-1	1	$-a_1$	$-b_1$	$-b_1$	a_1	a_1	b_1	b_1	$-a_1$	$-a_2$	$-b_2$	$-b_2$	a_2	a_2	b_2	b_2	$-a_2$		
$\sigma_v^{(4)}$	–	–	β_{n8}	1	-1	-1	1	$-a_1$	b_1	b_1	a_1	a_1	$-b_1$	$-b_1$	$-a_1$	$-a_2$	b_2	b_2	a_2	a_2	$-b_2$	$-b_2$	a_2		
$\sigma_v^{(5)}$	–	–	β_{n7}	1	-1	-1	1	$-a_2$	$-b_2$	$-b_2$	a_2	a_2	b_2	b_2	$-a_2$	$-a_1$	b_1	b_1	a_1	a_1	$-b_1$	$-b_1$	a_1		
$S_3^{(1)}$	–	η_6	β_{n4}	1	-1	1	-1	a_1	$-b_1$	b_1	a_1	$-a_1$	b_1	$-b_1$	$-a_1$	a_2	$-b_2$	b_2	a_2	$-a_2$	b_2	$-b_2$	$-a_2$		
$S_3^{(2)}$	–	η_{10}	β_{n10}	1	-1	1	-1	a_1	b_1	$-b_1$	a_1	$-a_1$	$-b_1$	b_1	$-a_1$	a_2	b_2	$-b_2$	a_2	$-a_2$	$-b_2$	b_2	$-a_2$		
$S_3^{(3)}$	–	η_8	β_{n8}	1	-1	1	-1	a_2	$-b_2$	b_2	a_2	$-a_2$	b_2	$-b_2$	$-a_2$	a_1	$-b_1$	b_1	a_1	$-a_1$	b_1	$-b_1$	$-a_1$		
$S_3^{(4)}$	–	η_9	β_{n2}	1	-1	1	-1	a_2	b_2	$-b_2$	a_2	$-a_2$	$-b_2$	b_2	$-a_2$	a_1	b_1	$-b_1$	a_1	$-a_1$	$-b_1$	b_1	$-a_1$		

Denotations: A_1 and A_2 – symmetry types, symmetrical and antisymmetrical with respect to reflection from vertical plane; E1 and E11 – doubly degenerated species of the same symmetry. Characteristic symmetry: C_{2y} – coordinates which do not change at reflection from horizontal and vertical planes; $C_{\sigma(y)}$ – coordinates which do not change at reflection from vertical plane; C_i – coordinates not having characteristic symmetry; $\cos\theta = a_1$; $\sin\theta = b_1$; $\cos 2\theta = a_2$; $\sin 2\theta = b_2$; $\theta = 72°$.

by the selection rules in the vibrational spectra of C_5H_{10} and C_5D_{10}. These force coefficient matrices are, in the general form, very complicated because of the numerous redundancy relations between the coordinates, and are not given here. The calculation of the force coefficients is considered below. The secular equations obtained by multiplication of the symmetrized matrices of the kinematic and the force coefficients were solved by iterative diagonalization.

3. The Raman spectra[2, 3–13] and the infrared absorption spectra[2, 4–13] of cyclopentane were repeatedly investigated. It should be noted that the data obtained by Bazhulin et al.[13] differ markedly from the results of other authors. According to reference 13, there are twice as many lines in the Raman spectrum (in the range extending to 1500 cm^{-1}) than observed by other authors. However, most of these new lines are very weak. The data concerning the polarization of lines, as given by different authors, differ somewhat. The results obtained by Fenske[12] by the photoelectric method should be given a greater weight.

Furthermore, there is a noticeable difference between the infrared spectrum of cyclopentane in the vapor and in the liquid phase, with respect to the number of bands and their position. Many of the bands of the vapor spectra are apparently overtones and combination frequencies, because the length of the cell (1 meter) used in reference 2 and the vapor pressure (220 mm) were quite large. Since the Raman spectra correspond to the liquid phase, it is proper to use the data of the infrared spectra for liquid, too.

The character of the observed Raman and infrared absorption spectra of cyclopentane agrees best with the selection rules for the group D_{5h} (see Table 1). As a matter of fact, there were 8 or 9 lines observed in the Raman spectra with frequencies under 1500 cm^{-1} that are of a noticeable intensity; only two of them are strongly polarized. In the infrared spectrum in this region, there are also only a few lines (5 or 6) of a noticeable intensity, some of which can be considered as combination frequencies. Furthermore, only very few frequencies of the Raman spectra coincide with the infrared bands. If cyclopentane belonged to the species C_{2v}, C_s, C_1, there would be 29 lines observed both in the infrared and in the Raman spectra; the frequencies in both spectra would have to coincide; and there should be 15 polarized Raman lines (C_{2v}, C_s) or 29 (C_1). The following considerations are also in favor of a planar structure of the ring C_5H_{10}. The angle ∠CCC, equal to 108 deg in a regular five-member ring, is close to the normal value of this angle in the paraffins (109°28′). The electron diffraction data[2] agree best with the model of a planar ring. In Table 3 the assignment is given for the vibration frequencies of C_5H_{10} and C_5D_{10}, based on model D_{5h}. In this

Table 3. Interpretation of Vibrational Spectra of Cyclopentane and of Deuterocyclopentane

	Cyclopentane							Deuterocyclopentane							
						Ref. 2		Ref. 5	Ref. 4				Ref. 2	Ref. 5	Ref. 4
No.	Coordinate	Symmetry	Calculated frequencies (cm^{-1})	Raman scattering (liquid)*	Infrared spectrum (liquid)†	D_{5h}	Nonplanar ring	D_{5h}	Nonplanar ring	Calculated frequencies (cm^{-1})	Raman scattering (liquid)	Infrared spectrum (liquid)	D_{5h}	Nonplanar ring	D_{5h}	Nonplanar ring
1	Q (C—C)	A_1'	871	886 (9) 0.12	—	886	886	886	886	784	802 (9) 0.5	—	802	802	802	802
2	α (HCH)	A_1'	1465	1487 (1) 0.5	—	1487	1487	1453	1487	1127	1124 (4) 0.6	—	1124	1124	1064	1124
3	q (C—H)	A_1'	2920	2906	—	2868	2868	2906	2868	2157	2132	—	2130	2130	2129	2108
4	β (CCH)	A_1''	1293	1295 (v. w.)	—	—	1306	(1150)	1020	925	—	943 (1)	—	943	—	722
5	β (CCH)	A_2''	1302	1311 (v. w.)	—	—	1316	(1250)	1206	1050	—	—	—	1060	—	—
6	β (CCH)	A_2''	575	—	546 (3)	1462	896	984	896	420	—	438 (1)	1066	1066	685	578
7	q (C—H)	A_2''	2974	—	2960 (10)	2965	2965	2960	2965	2228	—	2220 (10)	2230	2230	2220	2230
8, 9	Q (C—C)	E_1'	890	—	896 (8)	545	545 617	896	949	754	—	738 (8)	438	438	738	737
10, 11	β_{11_a} (CCH)	E_1'	1330	—	1316 (4)	896	1258	1316	1258	1168	—	1155 (3)	737	737	1155	1064
12, 13	α (HCH)	E_1'	1447	—	1456 (9)	1462	1462	1456	1462	1043	—	1064 (8)	1156	1156	1064	1156
14, 15	q (C—H)	E_1'	2911	—	2890 (10)	2876	2876	2890	2876	2141	—	2125 (10)	2125	2125	2125	2125
16, 17	β_{11_a} (CCH)	E_1''	720	717 (1)	—	1104	1104	1104	1090	469	—	—	778	778	778	778
18, 19	β_{11_b} (CCH)	E_1''	1210	1207 (3) 0.8	—	1207	1207	1207	717	962	937 (5) 0.9	—	965	965	937	530
20, 21	q (C—H)	E_1'	2973	2966 (9)	—	2966	2966	2966	2986	2224	2214 (6) 0.87	—	2214	2214	2214	2214
22, 23	γ (CCC)	E_2'	624	628 (v. w.)	—	283	827 769	589	1207	591	—	—	370	738 687	490	1064
24, 25	Q (C—C)	E_2'	1043	1030 (5) 0.82	—	1030	1030 949	1030	794	1081	1064 (3)	—	937	957 814	937	778
26, 27	β (CCH)	E_2'	1265	1253 (2) 0.8	—	1283	1283	1283	1283	893	—	—	1021	1021	1124	937
28, 29	α (HCH)	E_2'	1431	1453 (4) 0.72	—	1453	1453	1453	1453	1048	1021 (1)	—	1064	1064	1064	1124
30, 31	q (C—H)	E_2'	2904	2904 (4)	—	2944	2944	2904	2944	2134	2130 (2)	—	2130	2130	2130	2151
32, 33	r^{ee}	E_2''	282	283 (0?)	—	—	283 207	(283) (207)	283	258	270 (0)	—	—	270	—	270
34, 35	β_{11_a} (CCH)	E_2''	1021	1004 (v. w.)	—	—	984	(1000)	617	807	778 (1) 0.88	—	—	710	—	438
36, 37	β_{11_b} (CCH)	E_2''	1350	—	—	—	1033	(1150)	1104	1052	—	—	—	791	—	814
38, 39	q (C—H)	E_2''	2949	—	—	—	2900	(2950)	2965	2210	—	—	—	2150	—	2214

*Data from references 2, 12, and 13 for C_5H_{10}, and from reference 2 for C_5D_{10}.
†Data from reference 2.

interpretation, the conditions that are imposed by Table 1 were taken into consideration; the character of observed lines, the approximate range in which the frequencies of vibrations should be expected, in analogy with the spectra of the paraffins. Furthermore, for the assignment of frequencies the results of calculations of frequencies were used, based on the application of the force coefficients of the paraffins. The justification for this procedure follows from the following considerations. Since the angles and distances in C_5H_{10} differ little from the corresponding values in the paraffins, the force coefficients of C_5H_{10} must be nearly the same as the force coefficients in the paraffins. This supposition is well supported by calculations. After the assignment was made, some of the force coefficients (10) were recalculated more accurately; altogether, 30 frequencies were used for the calculation of these symmetrized coefficients. The agreement between the calculated and the observed frequencies was fairly good: the maximum deviation was 29 cm^{-1}, the mean error 11 cm^{-1}.

The assignment of the C—H frequencies should be mentioned especially. In the Raman spectrum of C_5H_{10} there are four strong polarized lines in the region 2800-3000 cm^{-1}, although, according to the selection rules, only one polarized line should be expected in this region. In the infrared spectrum there are two strong bands 2890 and 2960 cm^{-1}, that must be assigned to the symmetric and antisymmetric vibrations of the groups CH_2 $\nu_{14}^{E_1'}$ and $\nu_7^{A_2''}$. The frequency values of these bands indicate the approximate position of the C—H frequencies active in the Raman spectrum, because the calculated values of $\nu_{20}^{E_2'}$ and $\nu_{20}^{E_1''}$ are close to the values of $\nu_{14}^{E_1'}$ and $\nu_7^{A_2''}$. The value of $\nu_9^{A_1'}$ should be according to calculation, somewhat higher than that of $\nu_{14}^{E_1'}$. For the explanation of polarization and intensities of the four lines 2868, 2904, 2944, and 2966 cm^{-1} one has to assume that in this case the Fermi resonance is taking place between the overtones of the frequencies ν(HCH) and $\nu_9^{A_1'}$(C—H). The overtones have the following values: $2\nu_{20}^{E_2'}$ = 2906 (A_1'), $2\nu_{13}^{E_1'}$ = 2912(A_1'), and $2\nu_2^{A_1'}$ = 2974(A_1'). The lines 2868 and 2944 can be considered as a result of a resonance splitting $\nu_9^{A_1'}$ ~ 2906 cm^{-1} and $2\nu_{13}^{E_1'}$ (2912). The broad line 2904 results from the superposition of $\nu_{20}^{E_2'}$ ~ 2904 and of the polarized line $2\nu_{28}^{E_2''}$ (2906), and the broad line 2966 cm^{-1}

Table 4. Interpretation of Overtones and Combination Frequencies of C_5H_{10} and C_5D_{10}

Cyclopentane					Deuterocyclopentane		
Infrared spectrum*		Interpretation	Infrared spectrum		Interpretation	Infrared spectrum*		Interpretation
Liquid	Vapor		Liquid	Vapor		Liquid	Vapor	
—	617 (2)	$\nu_{10} - \nu_{24} = 599\ (A_2'')$	2560 (2)	—	$2\nu_{24} = 2566\ (E_1')$	—	502 (0)	$\nu_{18} - \nu_4 = 499\ (E_1'')$
—	697 (0)	$\nu_{10} - \nu_{23} = 688\ (E_1'')$	—	2610 (2)	$\nu_4 + \nu_9 = 2606\ (A_2'')$	—	578 (0)	$\nu_{13} - \nu_{24} = 585\ (A_2'')$
—	748 (0)	$\nu_{13} - \nu_{18} = 739\ (A_2'')$	2648	—	$\nu_{29} - \nu_{23} = 2647\ (E_1'')$†	—	686 (0)	$\nu_{18} - \nu_{19} = 686\ (A_2'')$
—	753 (0)	$\nu_{24} - \nu_{23} = 747\ (A_2'')$	2725 (1)	—	$\nu_{29} + \nu_{23} = 2736\ (E_1'')$	—	722 (1)	$\nu_{18} + \nu_{23} = 739\ (E_1'')$
778 (0)	770 (1)	$\nu_{10} - \nu_9 = 770\ (E_1'')$?	2753 (1)	—	$\nu_{13} + \nu_{28} = 2769\ (E_1')$	791 (0)	814 (1)	$\nu_{24} - \nu_{28} = 794\ (A_2'')$
817 (1)	827 (1)	$\nu_{29} - \nu_{23} = 825\ (E_1')$	2793 (2)	—	$\nu_4 + \nu_{19} = 2803\ (E_1'')$	—	935 (0)	$\nu_{18}\ (E_1'')$
964 (3)	949 (3)	$\nu_7 - \nu_9 = 941\ (A_2'')$	3202 (0)	3196 (0)	$\nu_{23} + \nu_{28} = 3213\ (E_1'')$	—	974 (0)	$\nu_{29} - \nu_{19} = 975\ (E_1')$
—	1020 (0)	$\nu_{29} - \nu_{23} = 1000\ (A_2'')$	3322	—	$\nu_{10} + 2\nu_{24} = 3324\ (E_1')$	997 (1)	—	$\nu_{14} - \nu_2 = 1001\ (E_1')$
1033 (1)	—	$\nu_{24}\ (E_1'')$	3481 (1)	3476 (1)	$\nu_2 + 2\nu_{20} = 3472\ (E_1')$	1111 (1)	1119 (1)	$\nu_{29} - \nu_{28} = 1109\ (E_1')$
—	1206 (0)	$\nu_{18}\ (E_1'')$	4065	—	$2\nu_2 + \nu_{13} = 4078\ (E_1')$	—	1315 (0)	$\nu_{14} - \nu_1 = 1323\ (E_1')$
1264 (3)	1258 (3)	$2\nu_{23} = 1256\ (E_1')$	4274	—	$\nu_{10} + \nu_{29} = 4282\ (A_2'')$	—	1458 (1)	$\nu_{29} - \nu_9 = 1476\ (E_1')$
—	1739 (0)	$\nu_{29} + \nu_{28} = 1736\ (A_2'')$				—	1510 (1)	$\nu_{24} + \nu_{18} = 1521\ (E_1')$
—	1884 (0)	$\nu_{29} - \nu_{24} = 1874\ (E_1')$	Raman scattering (liquid)**			—	1562 (1)	$\nu_2 + \nu_9 = 1562\ (A_2'')$
—	2021 (0)	$\nu_4 + \nu_{18} = 2012\ (E_1'')$				—	1772 (2)	$\nu_{29} - \nu_9 = 1778\ (E_1')$
—	2036 (1)	$\nu_{13} + \nu_{19} = 2036\ (A_2'')$				—	1887 (2)	$\nu_1 + \nu_{13} = 1866\ (E_1')$
—	2060 (1)	$2\nu_{24} = 2060\ (E_1')$				—	2005 (2)	$\nu_{13} + \nu_{14} = 2001\ (A_2'')$
—	2114 (0)	$\nu_9 + \nu_{18} = 2103\ (A_2'')$	257 (v. w.)			—	2099 (5)	$\nu_{10} + \nu_{14} = 2092\ (A_2'')$
2175 (1)	2181 (1)	$\nu_9 + \nu_{29} = 2179\ (E_1')$	750 (v. w.)		$\nu_9 - \nu_{23} = 263\ (E_1'')$	—	2155 (5)	$\nu_{10} + \nu_{29} = 2178\ (E_1')$ ‡
2288	—	$\nu_{23} + \nu_{24} = 2287\ (A_2'')$	1104 (v. w.)		$\nu_{24} - \nu_{23} = 747\ (E_1'')$	—	2203 (0)	$\nu_9 + \nu_{19} = 2205\ (E_1')$
—	2346 (1)	$\nu_{13} + \nu_{24} = 2346\ (E_1')$	1188 (w.)		$2\nu_9 = 1092\ (A_1')$	2283 (2)	—	$\nu_9 + \nu_{10} = 2279\ (E_1')$
—	2405 (0)	$\nu_{29} - \nu_9 = 2420\ (E_1'')$	1181 (w.)		$\nu_{23} - \nu_{23} = 1170\ (E_2'')$	—	3428 (2)	$\nu_{29} + \nu_{23} = 3400\ (A_2'')$
2475 (1)	2481 (1)	$\nu_{24} + \nu_{23} = 2483\ (E_1')$	1249 (w.)		$\nu_9 + \nu_{23} = 1179\ (E_2'')$	2900 (2)	—	$\nu_{29} + \nu_{24} = 2908\ (A_2'')$
2488	2482 (1)	$\nu_{13} + \nu_{24} = 2486\ (E_1')$	1263 (w.)		$2\nu_{28} = 1256\ (A_1')$	—	3000 (5)	$\nu_{29} + \nu_{24} = 2992\ (E_1')$
					$\nu_9 + \nu_{13} = 1263\ (E_2'')$			
						Raman scattering (liquid)*		
						2048 (2) 0.60		$2\nu_{28} = 2042\ (A_1')$
						2304 (2) 0.73		$2\nu_{19} = 2310\ (A_1')$

*Data from references 2 and 15.

**Data from reference 13.

†ν_{29} = 2930 cm^{-1}.

‡Fermi resonance $2\nu_{24}$ = 2128(E_1) with ν_{16}(E_1'').(?)

from superposition of $\nu_{20} \sim 2960\,cm^{-1}$ and $2\nu_9^{A_1'}$ (2974). Similarly, the two strong polarized lines 2108 and 2151 cm^{-1} C_9D_{10} are produced by a resonance splitting of $\nu_9^{A_1'} \sim 2132$ cm^{-1} and $2\nu_{13}^{E_1'} = 2128\,(A_1')$. The unpolarized line 2130 cm^{-1} must be assigned to $\nu_{30}^{E_2'}$. In this case there is no more superposition with the overtone $2\nu_{28}^{E_2'} = 2042\,cm^{-1}$. The overtone $2\nu_{28}^{E_2'}$ must be assigned to the polarized line 2048 cm^{-1}. The frequencies of the observed lines ν_{30} and ν_{20} are close to the frequencies of the infrared bands ν_{14} and ν_7, as it should be according to calculations. With the assignment of the fundamental frequencies, the rest of the observed lines (with a few exceptions) can be interpreted as overtones or combination frequencies (see Table 4).

Thus, the calculations lead to the conclusions that the Raman spectra and the infrared absorption spectra can be interpreted on the basis of the model D_{3h}. However, some features of the spectra do not preclude the possibility of an insignificant out-of-plane distortion of the carbon ring. Firstly, some of the forbidden lines, the approximate position of which can be determined by applying the force coefficients of the paraffins, have been observed in the spectrum of C_9H_{10} (ν_4, ν_{31}, $\nu_{25, 23}$, $\nu_{24, 22}$). They are very weak, however. Some of these frequencies (ν_4, $\nu_{22, 23}$, $\nu_{24, 25}$) appear also in the spectrum of C_9D_{10} as weak lines. Secondly, some of the lines of C_9H_{10} which we assign to the representation $E_1''E_2'$ and which must be depolarized ($\nu_{18, 19}$, $\nu_{24, 25}$, $\nu_{26, 27}$, $\nu_{22, 23}$) are slightly polarized, according to Fenske[13] (according to other authors, they are depolarized). Thirdly, most of the lines that we assign to the degenerated symmetry types are broad and diffuse. This can be explained by a small line splitting because of the removal of the degeneracy, if the ring is slightly bent. However, another explanation is also possible: the degenerate combination bands of molecules which are symmetrical tops may be broad, because the Q-branches of the separate sub-bands do not exactly coincide in frequency. Therefore, "the unresolved combination bands will appear as broad lines (bands) with a flat maximum".[35] Finally, the imperfect adherence of the observed frequencies of C_9H_{10} and C_9D_{10} to the product rules could also be explained by a small bending of the carbon ring.

APPENDIX

We have to consider here the recent paper by P. S. Lebedev[17] dealing with calculations of the vibrational spectra of cyclopentane and of C_5D_{10}. (We do not understand the appreciation expressed to one of us in this paper; the latter became known to us only after our paper had been submitted for publication).

The author also arrives at the same conclusion, that the symmetry D_{5h} is acceptable for cyclopentane; this conclusion, however, does not actually follow from his work, if the serious shortcomings occurring in it are taken into consideration. Firstly, the paper uses the erroneous assignment of frequencies by Tschambler and Voetter.[5] Secondly, the author did not calculate the system of force coefficients of C_9H_{10}; the force coefficients of other molecules were transferred unchanged. Therefore (and also mainly because of erroneous assignment) the discrepancies between the calculated and the observed frequencies are very large—100, 200, and even 300 cm^{-1}, exceeding by far the error limits for calculations of this kind. Thirdly, the paper does not consider vibrations of the species A_1'', A_2', and E_2''. Finally, there are errors in composing the matrices of the kinematic T^{-1} and of the force U coefficients. For instance, in the matrix T^{-1} for A_2'' the interaction (is given as) $T^{-1}(q_1q_1) = 1.0604$, although actually it is equal to 1.1208 (because this is an antisymmetric vibration). The calculated frequencies $\nu^{A_2''}$ (C—H) and $\nu^{A_2''}$ (C—D) therefore appeared lower by more than 100 cm^{-1}.

REFERENCES

1. J. Kilpatrick and K. Pitzer. J. Am. Chem. Soc. **69**, 2483 (1947).
2. F. Miller and R. Inskeep. J. Chem. Phys. **18**, 1519 (1950).
3. J. Aston and S. Schumann. J. Am. Chem. Soc. **65**, 341 (1943).
4. B. Curnutte and W. Shaffer. J. Mol. Spectroscopy **1**, 239 (1957).
5. H. Tschamler and H. Voetter. Monatsh. Chem. **83**, 1228 (1952).
6. M. V. Vol'kenshtein, M. A. El'iashevich, and B. I. Stepanov. "Kolebaniia molecul." (Vibrations of Molecules), Vol. I, GTTL, Moscow, 1949.
7. M. A. El'iashevich. Zhur. Eksp. i Teoret. Fiz. **13**, 651 (1943).
8. R. Wierl. Ann. Physik **8**, 521; Ann. Physik **13**, 453 (1932);
   L. Pauling and L. Brockway. J. Am. Chem. Soc. **59**, 1223 (1937);
   O. Hassel and H. Viervoll. Tidsskr. kjemi, Bergves. og metallurgi, **6**, 31 (1946).
9. K. Kohrausch and R. Seka. Chem. Ber. **69**, 729 (1936).
10. A. Reitz. Z. physik. Chem. B **33**, 179 (1936); Z. physik. Chem. B **38**, 381 (1938).
11. E. Rosenbaum and H. Jacobson. J. Am. Chem. Soc. **63**, 2841 (1941).
12. Fenske, Braun, Wiegand, and Rank. Anal. Chem. **19**, 700 (1947).
13. P. A. Bazhulin, Kh. E. Sterin, T. Bulanova, O. Solov'iova, N. Turova-Pollaki, and B. P. Kazanskii. Izv. Akad. Nauk USSR, Ser. Khim. 1, 7 (1946);
    G. S. Landsberg, P. A. Bazhulin, and M. M. Sushchinskii. "Osnovnye parametry spectrov kombinationnogo rasseianiia uglevodorodov." (Basic parameters in the Raman Spectra of Hydrocarbons), Academy of Sciences Press USSR, Moscow 1957.
14. P. Lambert and J. Lecompte. Ann. phys. **10**, 539 (1940).
15. E. Plyler, R. Stair, and C. Humphreys. J. Research Natl. Bur. Standards **38**, 211 (1947).
16. G. Herzberg. "Kolebatel'nye i vrashchatel'nye spectry mnogoatomnych molecul." (Vibrational and Rotational Spectra of Polyatomic Molecules), IL, Moscow 1949.
17. P. S. Lebedev. Opt. i Spektr. **6**, 154 (1959).

THEORY OF INTENSITIES IN THE INFRARED SPECTRA OF THE MOLECULES CF_4 AND C_2F_6

L. M. Sverdlov

Received 31 March 1959

The electro-optical parameters of the molecules CF_4 and C_2F_6 have been obtained in the first approximation of the valence-optical scheme. The absolute signs of all the parameters have been determined under the assumption that the negative end of the carbon-fluorine dipole is located on the fluorine atom. It is shown that the very large value of the derivative of the bond moment with regard to a variation of the bond length is the most characteristic property of the C—F bond.

1. We have previously[1-4] explained that it is necessary to use the first approximation of the valence-optical scheme[5] for the evaluation of intensities in the infrared spectrum of polyatomic molecules; in this approximation —contrary to the zero order approximation—one takes into consideration the interactions between different elements of the molecule. In particular, the methyl halogenides, which contain the bonds C—Cl, C—Br, and C—I, have been considered there.[3] It is also of interest to explain the polar properties of the C—F bonds. With this objective in mind, we have performed an evaluation of the electro ·tical parameters of the molecules CF_4 and C_2F_6.

The absolute integral intensities of the infrared spectra of the molecule CF_4 were measured by Schatz and Hornig.[6] The integral intensities of C_2F_6 were investigated in two papers by Crawford and his fellow-workers.[7,8] Errors committed in reference 7 were corrected in reference 8; the intensity of the low frequency band at 219 cm^{-1} was also determined there. In these papers the electro-optical parameters $\overline{\mu}_{CF}$ and $\partial\mu_{CF}/\partial q$ have been evaluated in the zero-order approximation of the valence-optical scheme. However, the results obtained there have no physical significance since these parameters have a different physical meaning for the symmetry types A_{2u} and E_u. Some of the frequencies have been incorrectly identified in reference 8: the frequency 522 cm^{-1} is ascribed there to the vibration β^{E_u} (CCF), and 219 cm^{-1} to the vibration α^{E_u} (FCF), while actually these identifications should be reversed.* The

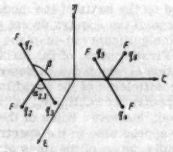
*One may verify this conclusion easily by using the force constants of the molecule CF_4 to estimate the frequency α(FCF) of the molecule C_2F_6.

experimental values of $\partial p/\partial Q_i$ for CF_4 and C_2F_6 according to references[6,8] are shown in Table 1.

2. For the evaluation of the molecules CF_4 and C_2F_6 we introduce normal vibrational coordinates—the variations of the bond lengths and of the angles q(C—F), β(CCF), and α(FCF) (see figure); and the valence-optical coordinates—the variations of the angles between the bonds and the axes $\beta_{n\xi}$, $\beta_{n\eta}$, $\beta_{n\zeta}$, which, in the case of the

Table 1. Experimental Values of $\partial p/\partial Q_i$ of the Molecules CF_4 and C_2F_6 (in units CGSE/cm $gm^{1/2}$)

CF_4				C_2F_6					
Symmetry	Frequency (cm^{-1})	$\frac{\partial p}{\partial Q_i}$		Symmetry	Frequency (cm^{-1})	$\frac{\partial p}{\partial Q_i}$	Symmetry	Frequency (cm^{-1})	$\frac{\partial p}{\partial Q_i}$
F_2	ν_3(C—F) 1283	219.8		A_{2u}	ν_7(C—F) 1116	184	E_u	ν_7(C—F) 1250	243
F_2	ν_4(FCF) 632	21.07		A_{2u}	ν_8(FCF) 714	68.1	E_u	ν_8(CCF) 219	17.5
							E_u	ν_9(FCF) 522	20.7



molecule C_2F_6, are expressed in terms of the independent valence-optical coordinates ϕ (the variations of the bond angles C—F along the axis ζ) and ψ (rotations of the bonds C—F around the axis ζ). The symmetry coordinates $S_k^{(\sigma)}$ for the vibrations, which are active in the infrared spectrum, are expressed in the following way in terms of the normal coordinates Q_i ($S_k^{(\sigma)} = \sum_b L_{kb} Q_i$):

$$q^{A_{2u}} = \sum_{i=3}^{6} C_{qi} Q_i;\quad \alpha^{A_{2u}} = \sum_{i=3}^{6} D_{\alpha i} Q_i;\quad \psi^{A_{2u}} = \sum_{i=5}^{6} E_i Q_i;$$

$$q^{E_u} = \sum_{i=7}^{9} C_{qi} Q_i;\quad \alpha^{E_u} = \sum_{i=7}^{9} D_{\alpha i} Q_i;\quad \beta^{E_u} = \sum_{i=7}^{9} D_{\beta i} Q_i;$$

$$\gamma^{E_u} = \sum_{i=7}^{9} E_i Q_i;\quad \psi^{E_u} = \sum_{i=7}^{9} F_i Q_i \text{ (for } C_2F_6),$$

where

$$E_i^{A_{2u}} = -D_{\alpha i}^{A_{2u}};\quad E_i^{E_u} = D_{\beta i}^{E_u};\quad F_i^{E_u} = \frac{1}{3} D_{\beta i}^{E_u} - \frac{2}{3} D_{\alpha i}^{E_u};$$

$$q^{F_2} = \sum_{i=3}^{4} C_i Q_i;\quad \alpha^{F_2} = \sum_{i=3}^{4} D_i Q_i \text{ (for } CF_4). \qquad (1)$$

In the first-order approximation of the valence optical scheme the derivatives $\partial P/\partial Q_i$ are given by the expressions:

$$\frac{\partial P_\zeta}{\partial Q_i^{A_{2u}}} = \sum \frac{\partial P}{\partial S_k^{A_{2u}}} L_{ki}$$

$$= \left\{ \left[-\sqrt{\frac{2}{3}} \left(\frac{\partial \mu_{CF}^{(1)}}{\partial q_1} + 2\frac{\partial \mu_{CF}^{(2)}}{\partial q_1} - \frac{\partial \mu_{CF}^{(4)}}{\partial q_1} - 2\frac{\partial \mu_{CF}^{(5)}}{\partial q_1} \right) \right.\right.$$

$$- \frac{4}{\sqrt{3}} \mu_{CF} \left(\frac{\partial r_1}{\partial q_1} + 2\frac{\partial r_2}{\partial q_1} - \frac{\partial r_4}{\partial q_1} - 2\frac{\partial r_5}{\partial q_1} \right) \Big] C_{qi}$$

$$+ \left[-\frac{4}{\sqrt{3}} \frac{\mu_{CF}}{r_{CF}} - \frac{4}{\sqrt{6}} \left(\frac{\partial \mu_{CF}^{(1)}}{\partial r_1} + 2\frac{\partial \mu_{CF}^{(2)}}{\partial r_1} \right.\right.$$

$$\left.\left. - \frac{\partial \mu_{CF}^{(4)}}{\partial r_1} - 2\frac{\partial \mu_{CF}^{(5)}}{\partial r_1} \right) \frac{1}{r_{CF}} \right] E_i \Big\}; \qquad (2a)$$

$$\frac{\partial P_\xi}{\partial Q_i^{A_{2u}}} = \frac{\partial P_\eta}{\partial Q_i^{A_{2u}}} = 0 \quad (i = 5, 6).$$

$$\frac{\partial P_\eta}{\partial Q_i^{E_u}} = \sum \frac{\partial P}{\partial S_k^{E_u}} L_{ki}$$

$$= \left\{ \left[2\sqrt{\frac{2}{3}} \left(\frac{\partial p_{CF}^{(1)}}{\partial q_1} - \frac{\partial p_{CF}^{(3)}}{\partial q_1} - \frac{\partial p_{CF}^{(4)}}{\partial q_1} + \frac{\partial p_{CF}^{(2)}}{\partial q_1} \right) - \frac{1}{\sqrt{3}} \frac{p_{CF}}{r_{CF}} \right.\right.$$

$$\left.\left. \left(\frac{\partial r_1}{\partial q_1} - \frac{\partial r_2}{\partial q_1} - \frac{\partial r_3}{\partial q_1} + \frac{\partial r_4}{\partial q_1} \right) \right] G_{ji} \right.$$

$$+ \left[-\frac{1}{\sqrt{3}} \frac{p_{CF}}{r_{CF}} + 4\sqrt{\frac{2}{3}} \left(\frac{\partial p_{CF}^{(1)}}{\partial r_1} - \frac{\partial p_{CF}^{(3)}}{\partial r_1} - \frac{\partial p_{CF}^{(4)}}{\partial r_1} \right.\right.$$

$$\left.\left. + \frac{\partial p_{CF}^{(2)}}{\partial r_1} \right) \frac{1}{r_{CF}} \right] E_i + \left[-2\sqrt{\frac{2}{3}} \frac{p_{CF}}{r_{CF}} \right| F_i \Big\} \qquad (2b)$$

and

$$\frac{\partial P_\zeta}{\partial Q_i^{E_u}} = \frac{\partial P_\zeta}{\partial Q_i^{A_{2u}}} = 0 \quad (i = 7, 8, 9); \text{ (for } C_2F_6).$$

$$\frac{\partial P_\zeta}{\partial Q_i^{F_2}} = \frac{2}{\sqrt{3}} \left(\frac{\partial p_{CF}^{(1)}}{\partial q_1} - \frac{\partial p_{CF}^{(2)}}{\partial q_1} \right) C_i - \frac{2}{\sqrt{3}} \frac{p_{CF}}{r_{CF}} D_i; \qquad (3)$$

$$\frac{\partial P_\xi}{\partial Q_i^{F_2}} = \frac{\partial P_\eta}{\partial Q_i^{F_2}} = 0 \quad (i = 3, 4) \text{ (for } CF_4).$$

A mechanical problem was solved in order to determine the coefficients D and C of the molecules CF_4 and C_2F_6. The force constants were chosen in such a way that the respective constants for CF_4 and C_2F_6 did not differ appreciably from each other, nor from the values determined by Stepanov[8] for the fluorine substitutes of methane (see Table 2). An iteration method due to Mayants[9] was used to solve the secular equations; this method permitted also a determination of the vibration form. In Table 3 the matrix coefficients L_{kl} are given. To verify the numerical values of the coefficients L_{kl} the matrix relation

$$|L_{ik}| \cdot |L_{ij}^{-1}| = |A_{ij}|,$$

has been used where $\| A_{ij} \|$ is the matrix of the potential coefficients. The formulas (1) were used to obtain the coefficients E_i and F_i. The coefficients L_{ik}^{-1}, which one needs to determine the derivatives of the dipole moment with regard to the symmetry coordinates, are given in

Table 2. Symmetrized Matrices of the Force Constants for CF_4 and C_2F_6 (in units of 10^5 cm^{-2})

F_2	q	α	A_{2u}	q	α	E_u	q	β	α
q	14.6129	2.8284	q	14.5	1.3	q	11.7	1.7	−1.5
α	2.8284	1.6574	α	1.3	2.9	β	1.7	1.25	−0.1
						α	−1.5	−0.1	1.35

Table 3. Matrices of the Coefficients $L_{kl}(C_l, D_l)$ for C_2F_6 (in units of $(AEM^{-1})^{1/2}$)

A_{2u}	Q_8	Q_9	E_u	Q_7	Q_8	Q_9
q	0.2723	0.0791	q	0.4091	−0.0343	0.0079
α	−0.3902	0.3501	β	−0.0767	0.2458	0.0187
			α	0.3781	−0.0283	0.458

Table 4. Matrices of the Coefficient $L_{ik}^{-1}(C_i^{-1}, E_i^{-1}, F_i^{-1})$ of the Molecules CF_4 and C_2F_6 (in units 10^{-12} $gm^{1/2}$)

F_2	q	α	A_{2u}	q	γ	E_u	q	γ	β
Q_3	3.5005	0.3434	Q_6	3.5744	0.8077	Q_7	3.3513	0.4241	0.1075
Q_4	3.1954	2.5753	Q_9	3.9839	−2.7802	Q_8	1.1985	5.2982	0.2728
						Q_9	−2.6986	1.3584	−4.2929

Table 4. These derivatives were obtained from the formulas

$$\frac{\partial P}{\partial S_k^{(\alpha)}} = \sum_i \frac{\partial P}{\partial Q_i} L_{ik}^{-1}$$

for different combinations of the signs of $\partial P/\partial Q_i$ (see Table 5); the data from Table 1 for $\partial P/\partial Q_i$ and from Table 4 for L_{ik}^{-1} were used for this purpose. Combining the derivatives $\partial P/\partial S^{A_{2u}}$ and $\partial P/\partial S^{E_u}$ we obtain expressions for the electro-optical parameters

$$\left[\frac{\partial p_{CF}^{(1)}}{\partial q_1} \right], \left[\frac{\partial p_{CF}^{(3)}}{\partial q_1} \right], \left[\frac{\partial p_{CF}^{(1)}}{\partial r_1} \right], \left[\frac{\partial p_{CF}^{(3)}}{\partial r_1} \right], \frac{p_{CF}}{r_{CF}}.$$

In Tables 6 and 7 the numerical values of these parameters are given for the molecules C_2F_6 and CF_4 for different combinations of the signs of $\partial P/\partial Q_i$. To choose the correct numerical values of the electro-optical parameters criteria were used which had been formulated in the preceding paper.[4] These conditions are the following:

(i) $$\left| \frac{\partial p_{CF}^{(1)}}{\partial q_1} \right| \geqslant \left| \frac{\partial p_{CF}^{(2)}}{\partial q_1} \right|; \quad \left| \frac{\partial p_{CF}^{(1)}}{\partial r_1} \right| \geqslant \left| \frac{\partial p_{CF}^{(2)}}{\partial r_1} \right|;$$

(ii) $|\partial\overline{\mu}/\partial\phi|$ should have a minimum value; (iii) $\partial\mu^{(1)}/\partial q_1$ and the dipole moment of the bond, $\mu^{(1)}$, should have opposite signs.

The best way to fulfill these criteria in the case of the molecule C_2F_6 is to choose the fifth combination:

$$+\frac{\partial P}{\partial Q_5}, -\frac{\partial P}{\partial Q_6}, -\frac{\partial P}{\partial Q_7}, -\frac{\partial P}{\partial Q_8}, +\frac{\partial P}{\partial Q_9}.$$

In Table 8 a system of electro-optical parameters

Table 5. Derivatives of the Dipole Moment with Regard to Symmetry Coordinates ∂p/∂S (in units Debye/Angstrom)

Molecule	Symmetry E_u	Signs of $\frac{\partial p}{\partial Q_{7,8,9}}$			
		− − −	− − +	− + −	− + +
C_2F_6	$\frac{\partial p}{\partial q}$	−7.7135	−8.9027	−7.2948	−8.5739
	$\frac{\partial p}{\partial r}$	−2.28	−1.8356	−0.4256	0.2188
	$\frac{\partial p}{\partial \gamma}$	+0.7084	−1.3264	0.8039	−1.2309

Table 5 - continued

Symmetry A_{2u}	Signs of $\frac{\partial p}{\partial Q_{5,6}}$		Molecule	Symmetry F_2	Signs of $\frac{\partial p}{\partial Q_{3,4}}$	
	+ +	+ −			− −	− +
$\frac{\partial p}{\partial q}$	9.39	3.8639	CF_4	$\frac{\partial p}{\partial q}$	−8.3674	−7.0208
$\frac{\partial p}{\partial r}$	−0.4071	3.3796		$\frac{\partial p}{\partial \alpha}$	−1.0775	0.0077

of the molecule C_2F_6 which corresponds to this combination is given. For the molecule CF_4 one has to choose the first combination:

$$-\frac{\partial P}{\partial Q_3}, \quad -\frac{\partial P}{\partial Q_4}.$$

There is sufficient justification for the assumption that the negative end of the C—F bond dipole is located on the fluorine atom (since the electronegativity of the fluorine atom is larger than that of the carbon atom). A positive sign of μ_{CF} corresponds to this assumption. The fulfilment of this condition for all the electro-optical parameters implies the absolute signs given in the Tables 7 and 8.

3. The numerical values obtained for the bond moments μ_{CF} of the molecules CF_4 and C_2F_6 agree well with the values of μ_{CF} obtained for the molecules CH_3F, CH_2F_2, CHF_3 (1.25–1.12 Debye) on the basis of the additive scheme (it is assumed there that μ_{CH} has approximately the same value in these compounds as in the methyl halogenides CH_3Cl, CH_3Br, and CH_3I, that is, about 0.5 Debye); for the dipole moments of the molecules CH_3F, CH_2F_2, and CHF_3 the values obtained from microwave-spectroscopical data[10] have been used.

A comparison of the parameters of the molecule CF_4, that is,

$$\frac{\mu_{CF}}{r_{CF}} \text{ and } \left(\frac{\partial p_{FC}^{(1)}}{\partial q_1} - \frac{\partial p_{CF}^{(2)}}{\partial q_1}\right)$$

Table 6. Electro-Optical Parameters of the Molecule C_2F_6 (in units Debye/Angstrom) for Various Combinations of the Signs of $\partial p/\partial Q_{5,6}$ and $\partial p/\partial Q_{7,8,9}$

Parameter	Signs of $\frac{\partial p}{\partial Q_{7,8,9}}$ (upper) $\frac{\partial p}{\partial Q_{5,6}}$ (lower)							
	− − − + + +	− − − + − −	− − − − − −	− − − − − +	− − + + + −	− − + + − +	− − + − − −	− − + − − +
$\left[\frac{\partial p_{CF}^{(1)}}{\partial q_1}\right]$	−6.9417	−4.7265	0.6436	−1.5716	−7.4839	−5.2487	0.1214	−2.0938
$\left[\frac{\partial p_{CF}^{(2)}}{\partial q_1}\right]$	−2.2181	−0.0029	5.3672	3.152	−1.957	0.2582	5.6283	3.4131
$\frac{1}{r_{CF}}\left[\frac{\partial p_{CF}^{(1)}}{\partial q_1}\right]$	−0.2289	−1.0019	−0.3051	0.3778	−0.5979	−1.3109	−0.7041	0.0688
$\frac{1}{r_{CF}}\left[\frac{\partial p_{CF}^{(2)}}{\partial q_1}\right]$	0.5459	0.3797	−0.2271	1.1526	−0.1807	−0.9537	−0.3469	0.426

Parameter	− + − + + +	− + − − + −	− + − − − −	− + − + − +	− + + + + −	− + + − + −	− + + − − −	− + + − − +
$\left[\frac{\partial p_{CF}^{(1)}}{\partial q_1}\right]$	−6.7707	−4.5555	0.8146	−1.4007	−7.2929	−5.0777	0.2924	−1.9229
$\left[\frac{\partial p_{CF}^{(2)}}{\partial q_1}\right]$	−2.3036	−0.0884	5.2817	3.0685	−2.0425	0.1727	5.5428	3.3276
$\frac{1}{r_{CF}}\left[\frac{\partial p_{CF}^{(1)}}{\partial q_1}\right]$	0.1703	−0.6027	0.0041	0.777	−0.1387	−0.9117	−0.3049	0.468
$\frac{1}{r_{CF}}\left[\frac{\partial p_{CF}^{(2)}}{\partial q_1}\right]$	0.3876	−0.3853	0.2214	0.9044	−0.339	−1.1119	−0.5052	0.2678

Parameter	Signs of $\frac{\partial p}{\partial Q_{7,8,9}}$			
	− − −	− + +	− + −	− + +
$\frac{\mu_{CF}}{r_{CF}}$	−0.4338	0.8122	−0.4923	0.7538

and of the corresponding parameters of the molecule C_2F_6,

$$\frac{\mu_{CF}}{r_{CF}} \text{ and } \left\{\left[\left(\frac{\partial p_{CF}^{(1)}}{\partial q_1} - \frac{\partial p_{CF}^{(2)}}{\partial q_1}\right) - \left(\frac{\partial p_{CF}^{(1)}}{\partial q_1} - \frac{\partial p_{CF}^{(2)}}{\partial q_1}\right)\right] - \frac{1}{\sqrt{2}} r_{CF}\left[\left(\frac{\partial r_{F1}}{\partial q_1} - \frac{\partial r_{F4}}{\partial q_1}\right) - \left(\frac{\partial r_{F3}}{\partial q_1} - \frac{\partial r_{F5}}{\partial q_1}\right)\right]\right\} = -5.5069 \frac{\text{Debye}}{\text{Angstrom}}$$

shows that there is a noticeable increase in the polarity of the bond C—F in the molecule CF_4.

A comparison of the numerical values of μ_{CF}/r_{CF} and $[\partial\mu_{CF}^{(1)}/\partial q_1]$ of the molecule C_2F_6 with the corresponding values of various bond parameters of the molecules previously studied by the author[1-4] (C_2H_4, C_2H_2, CH_4, CH_3Cl, CH_3Br, CH_3I, NH_3, PH_3, and SO_2) leads to the conclusion that a very large value of the derivative of the dipole moment with regard to a variation of the bond length is the most characteristic property of the C—F bond. This explains the appearance of strong infrared bands which correspond to the stretching vibrations of the C—F bond.

It appeared in the evaluation of the methyl halogenides[2] CH_3I, CH_3Br, and CH_3Cl that an increase of the electronegativity of the halogen atom X implied a corresponding increase of the electro-optical parameters $[\partial\mu_{CX}^{(1)}/\partial q_1]$ and μ_{CX}/r_{CX}; particularly noticeable is the increase of the parameter $[\partial\mu_{CX}^{(1)}/\partial q_1]$. This conclusion is further confirmed by the results of this paper although the value of μ_{CF}/r_{CF} for the molecule C_2F_6 is almost the same as the value of μ_{CCl}/r_{CCl}, but $[\partial\mu_{CF}^{(1)}/\partial q_1]$ is about three times larger than $[\partial\mu_{CCl}^{(1)}/\partial q_1]$. This, in particular, reveals the large electronegativity of the fluorine atom.*

*However, one has to consider that the so much larger value of $\partial\mu_{CF}^{(1)}/\partial q_1$ for the molecules C_2F_6 and CF_4 as compared with the value $\partial\mu_{CCl}^{(1)}/\partial q_1$ of the molecule CH_3Cl could be partially related to the presence of several atoms of fluorine in CF_4 and C_2F_6, while there is only one atom of chlorine in CH_3Cl.

Table 7. Electro-Optical Parameters of the Molecule CF_4 (in units Debye/Angstrom)

Parameter	Signs of $\frac{\partial p}{\partial Q_{3,4}}$	
	− −	− +
$\left(\frac{\partial p_{CF}^{(1)}}{\partial q_1} - \frac{\partial p_{CF}^{(2)}}{\partial q_1}\right)$	−7.2463	−6.0802
$\frac{\mu_{CF}}{r_{CF}}$	0.9332	−0.0067
μ_{CF} (Debye units)	1.2691	−0.0091

Table 8. Electro-Optical Parameters of the Molecule C_2F_6 (in units Debye/Angstrom)

μ_{CF} (Debye units)	1.1048
$\frac{\mu_{CF}}{r_{CF}}$	0.8122
$\left\{\left(\frac{\partial p_{CF}^{(1)}}{\partial q_1} - \frac{\partial p_{CF}^{(2)}}{\partial q_1}\right) + \frac{\sqrt{2}}{2} r_{CF}\left[\left(\frac{\partial r_{F1}}{\partial q_1} - \frac{\partial r_{F4}}{\partial q_1}\right) + 3\left(\frac{\partial r_{F3}}{\partial q_1} - \frac{\partial r_{F5}}{\partial q_1}\right)\right]\right\}$	−7.4839
$\left\{\left(\frac{\partial p_{CF}^{(1)}}{\partial q_1} - \frac{\partial p_{CF}^{(2)}}{\partial q_1}\right) + \frac{\sqrt{3}}{4} r_{CF}\left[3\left(\frac{\partial r_{F1}}{\partial q_1} - \frac{\partial r_{F4}}{\partial q_1}\right) + 5\left(\frac{\partial r_{F3}}{\partial q_1} - \frac{\partial r_{F5}}{\partial q_1}\right)\right]\right\}$	−1.957
$\frac{1}{r_{CF}}\left(\frac{\partial p_{CF}^{(1)}}{\partial q_1} - \frac{\partial p_{CF}^{(2)}}{\partial q_1}\right)$	−0.5379
$\frac{1}{r_{CF}}\left(\frac{\partial p_{CF}^{(1)}}{\partial q_1} - \frac{\partial p_{CF}^{(2)}}{\partial q_1}\right)$	−0.1807

Table 9. Electro-Optical Parameters of the Molecule C_2F_6 (in units Debye/Angstrom) based on Crawford's Interpretation[8] and Simanouti's Values of the Force Constants[11]

Parameter	Signs of $\frac{\partial p}{\partial Q_{7,8,9}}$ (upper) / $\frac{\partial p}{\partial Q_{5,6}}$ (lower)							
	+++ / ++	+++ / +−	+++ / −−	+++ / −+	+−− / ++	+−+ / +−	+−− / −−	+−− / −+
$\left[\frac{\partial \mu_{CF}^{(1)}}{\partial q_1}\right]$	1.5332	−0.8839	3.808	6.225	1.3728	−1.0442	3.6476	6.0747
$\left[\frac{\partial \mu_{CF}^{(2)}}{\partial q_1}\right]$	−2.4727	−4.8897	−0.1979	2.2192	−2.3025	−4.8098	−0.1177	2.2993
$\frac{1}{r_{CF}}\left[\frac{\partial \mu_{CF}^{(1)}}{\partial q_1}\right]$	0.7313	−0.0128	−0.8414	−0.0973	0.3403	−1.2254	−0.3948	−0.4793
$\frac{1}{r_{CF}}\left[\frac{\partial \mu_{CF}^{(2)}}{\partial q_1}\right]$	−0.0986	−0.8427	−1.6713	−0.9271	0.0997	−1.4731	−0.6445	−0.7289

Parameter	Signs of $\frac{\partial p}{\partial Q_{7,8,9}}$			
	+++	++−	+−+	−++
$\frac{\mu_{CF}}{r_{CF}}$	1.2904	1.2902	0.0484	−0.0382

Finally, let us consider another question. We have mentioned above that the two bands 219 and 522 cm^{-1} have been wrongly interpreted in Crawford's paper.[8] This interpretation has been used by Simanouti[11] in his evaluation of the force constant, and his values were again used by Crawford to calculate the coefficients L_{kl}^{-1}. We have calculated the electro-optical parameters of the molecule C_2F_6 in the first approximation of the valence-optical scheme, using the interpretation and the coefficients L_{kl}^{-1} of Crawford. The results obtained are shown in Table 9 (we do not quote there the combinations which lead to very small values of μ_{CF}). It appears from this table that not one of these combinations satisfies the criteria formulated above. A wrong interpretation leads thus to erroneous values of the electro-optical parameters. This circumstance appears of considerable interest, since it shows the availability of a supplementary method for the confirmation of the correct interpretation of observed bands in the infrared spectra of polyatomic molecules.

REFERENCES

1. L. M. Sverdlov. Opt. i Spektr. 4, 697 (1958).
2. L. M. Sverdlov. Opt. i Spektr. 6, 729 (1959).
3. L. M. Sverdlov. Opt. i Spektr. 7, 21 (1959).
4. L. M. Sverdlov. Opt. i Spektr. 7, 152 (1959).
5. M. V. Volkenshtein, M. A. El'yashevich, and B. I. Stepanov. "Molecular Vibrations." GITTL, Moscow, 1949.
6. P. N. Schatz and D. F. Hornig. J. Chem. Phys. 21, 1516 (1953).
7. D. Q. Williams, W. B. Person, and B. Crawford. J. Chem. Phys. 23, 179 (1955).
8. J. Mills, W. Person, J. Schere, and B. Crawford. J. Chem. Phys. 28, 851 (1958).
9. L. S. Mayants. Trudy Fiz. Inst. Akad. Nauk 5, 63 (1950).
10. W. Gordy, W. V. Smith, and R. F. Trambarulo. "Microwave Spectroscopy." GITTL, Moscow, 1955.
11. T. Simanouti. J. Chem. Phys. 17, 848 (1949).

LAWS OF THE ABSORPTION OF INFRARED RADIATION IN THIN LAYERS OF SOME GASES I. COEFFICIENT OF ABSORPTION IN VIBRATION-ROTATION BANDS

P. I. Bresler

Received 19 March 1959

The laws of absorption of infrared radiation in gases for thicknesses of layers, which are generally dealt with in infrared absorption instruments, are examined. Approximate formulas for the determination of the coefficient of absorption and of the absorbed radiation in vibration-rotation bands of diatomic and some more complicated molecules are investigated.

INTRODUCTION

A large number of works have been devoted to the solution of the problem of the absorption of infrared radiation in gases. Amongst these and having significant interest are the works of Elsasser[1] who has investigated the absorption of radiation in a schematic band, consisting of an infinite succession of completely identical equidistant absorption lines, having the Lorentz form. The results obtained by him qualitatively describe many properties of absorption bands; however, for quantitative calculations, it is impossible to apply immediately the formulas of Elsasser since they do not include some quantities characterizing the properties of actual gas molecules.

In other works, for example reference 2, the determination of the laws of absorption for actual gases is produced by way of a selection of empirical formulas, suitable only for conditions coinciding with the conditions of the experiment.

In the present work an attempt is made to determine the general laws of absorption in thin layers of a gas for groups of molecules, the vibration-rotation bands of which can be described by comparatively simple schemes, differing from Elsasser's scheme in the manner of the function of the distribution of intensity of the rotational (equidistant) lines in the dependence on their positions in the band. Some of the results obtained are based on the appropriate application of the formulas of Elsasser, and the conditions and limits of applicability of the latter to absorption bands of the examined type are defined.

GENERAL EXPRESSION FOR THE ABSORPTION COEFFICIENT

Vibration-rotation absorption bands of many gases can be approximately examined in the sense of a system of equidistant bands of Lorentz form, having different

intensities. The absorption coefficient $K(\nu)$ of such a system is given by

$$K(\nu)=\sum_{n=-\infty}^{n=+\infty}K_n(\nu)=\sum_{n=-\infty}^{n=+\infty}\frac{\pi^{-1}\cdot a_n\cdot\delta_n}{(\nu-\nu_{0_n})^2+\delta_n^2}, \quad (1, I)$$

where

$$a_n=\int_0^\infty K_n(\nu)\,d\nu$$

is the integrated intensity of the nth line; ν_{0_n} is the frequency, appropriate to the center of the nth line; and δ_n is the half-width of the nth line. In the limits of a single vibration-rotation band it is possible to assume that $\delta_n = \delta = \text{const}$.

Absorption bands of diatomic, linear, nonsymmetric molecules, and also of linear symmetric molecules of the type CO_2 (with alternation of the statistical weights of the rotational levels 1;0;1;0...) can be approximately presented in the sense of two groups (branches) of equidistant bands, symmetrically located relative to the frequency of the vibrational transition ν_0 (the center of the band).

The intensities of bands in the branches obey the approximate formula.*

*Actually, the intensities of the bands in each of the branches obey different formulas.

For the R branch: $a_n = a_0\cdot(2pn+2)\,e^{-\frac{Bhc}{kT}pn(pn+1)}$.

For the P branch: $a_n = a_0\cdot 2pn\cdot e^{-\frac{Bhc}{kT}pn(pn+1)}$.

However, it is possible to show that in the calculation of the integrated absorption of the radiation in the band we can neglect the asymmetry of the branches.

$$a_n\cong a_0\cdot(2pn+1)\cdot e^{-\frac{Bhc}{kT}pn(pn+1)}, \quad (2, I)$$

where B is the rotational constant of the molecule; p = 1 for diatomic and linear nonsymmetric molecules; p = 2 for molecules with forbidden odd rotational levels; a_0 is the integrated intensity of the line with n = 0.

It is not difficult to show that $a_0 = (p/2)(Bhc\alpha/kT)$ where α is the integrated intensity of the whole band, independent of large changes in temperature and pressure.

The position of the centers of the bands, ν_{0_n}, in the branches is approximately defined by the next formula

$$\nu_{0_n}=\nu_0+2Bpn, \quad (3, I)$$

where ν_0 is the center of the band.*

*Expression (3, I) is written with the assumption that the line with n = 0 coincides with the center of the band ν_0.

Putting (3, I) and (2, I) into (1, I), we obtain

$$K(\nu-\nu_0)=\sum_{n=-\infty}^{n=+\infty}\frac{\pi^{-1}\cdot a_0\cdot\delta\cdot(2p|n|+1)\cdot e^{-\frac{Bhc}{kT}p|n|(p|n|+1)}}{(\nu-\nu_0+2Bpn)^2+\delta^2}. \quad (4, I)$$

The infinite series (4, I) does not yield to an immediate analytical summation. For the determination of the possibility of an approximate calculation $K(\nu-\nu_0)$ it is expedient to examine series (4, I) separately, both far from the center of the band ν_0 (for large values of the argument $\nu-\nu_0$), and close to its center.

THE ABSORPTION COEFFICIENT FAR FROM THE BAND CENTER

Let us examine again series (4, I) for large values of the argument $(\nu-\nu_0)$. We will look for a solution for the function of the assignment of the intensities of the rotational lines in the band $f(|n|)$ of arbitrary type, restricted only by certain conditions:

1. $f(|n|)$ is arbitrary, even, continuous, and for large values of n a progressively decreasing function;
2. $\lim_{|n|\to\infty} f(|n|)=0$;
3. $\sum_{n=-\infty}^{n=+\infty} n^r\cdot f(|n|)\cong\int_{-\infty}^{+\infty} x^r\cdot f(|x|)\,dx=2\int_0^\infty x^r\cdot f(x)\,dx$,

where r is an arbitrary, even, whole number.

Conditions 1 and 2 lead to the obvious fulfillment of the necessary and sufficient condition of convergence of the series.

$$K(\nu-\nu_0)=\sum_{n=-\infty}^{n=+\infty}\frac{\pi^{-1}\cdot a_0\cdot\delta\cdot f(|n|)}{(\nu-\nu_0+2Bpn)^2+\delta^2}. \quad (5, I)$$

Series (4, I) appears, obviously, as a particular case of series (5, I). The three conditions indicated above are generally observed in real bands.

It is possible to show that function (5, I) has, for large values of the argument $\nu-\nu_0$, an asymptotic solution of the following type:

$$K(\nu-\nu_0)\sim\frac{2\pi^{-1}\cdot a_0\cdot\delta}{(\nu-\nu_0)^2}\sum_{t=0}^{\infty}(2t+1)\cdot\left[\frac{2Bp}{\nu-\nu_0}\right]^{2t}\cdot\int_0^\infty f(x)\cdot x^{2t}\cdot dx. \quad (6, I)$$

For an approximate calculation of the function $K(\nu-\nu_0)$ one should take several of the initial, decreasing terms of the asymptotic solution. In particular, when it is possible to limit oneself to only the first term of the asymptotic approximation, we get

$$K(\nu-\nu_0)\cong\frac{2\pi^{-1}\cdot a_0\cdot\delta}{(\nu-\nu_0)^2}\cdot\int_0^\infty f(x)\,dx.$$

Taking into account that

$$2a_0\cdot\int_0^\infty f(x)\,dx=a,$$

where a, as before, is the integrated intensity of the entire band, we have

$$K(\nu-\nu_0)\cong\frac{\pi^{-1}\cdot a\cdot\delta}{(\nu-\nu_0)^2}. \quad (7, I)$$

Formula (7, I) shows that far from its center the absorption band behaves like a separate line of the Lorentz form with an intensity equal to the integrated intensity of the whole band. From the deduction of formula (7, I) it is clear that it is applicable for bands having only P and R branches as well as for bands having a Q branch. It is not difficult to show, that this formula is also valid for asymmetric bands, for which $f(n)\neq f(-n)$.

For the examined case

$$f(|n|)=(2p|n|+1)\cdot e^{-mp|n|(p|n|+1)},$$

where m = Bhc/kT, the asymptotic solution (6, I) leads to the following expression:

$$K(\nu-\nu_0)\sim\frac{\pi^{-1}\cdot\alpha\cdot\delta}{(\nu-\nu_0)^2}\cdot\sum_{l=0}^{\infty}(2l+1)\cdot\left[\frac{4B^2}{m(\nu-\nu_0)^2}\right]^l$$
$$\times\left\{\sum_{\tau=0}^{\infty}m^\tau\cdot\frac{(l+\tau)!}{(2\tau)!}\cdot\left[1-\frac{m}{2(2\tau+1)}\right]-\frac{i\cdot\sqrt{\pi m}}{2^l}\right.$$
$$\left.\times\sum_{\tau=0}^{\infty}\left(\frac{m}{2}\right)^\tau\cdot\frac{(2l+2\tau-1)!!}{(2\tau+1)!}\right\}. \qquad (8,\ I)$$

In the majority of cases of interest to us $m \ll 1$, so that in the summation over τ it is generally possible to limit oneself to the term with $\tau = 0$. Using this condition, we obtain the asymptotic approximation for the function $K(\nu - \nu_0)$

$$K(\nu-\nu_0)\simeq\frac{\pi^{-1}\cdot\alpha\cdot\delta}{(\nu-\nu_0)^2}\cdot\sum_{l=0}^{N}(2l+1)\cdot\left[\frac{4B^2}{m(\nu-\nu_0)^2}\right]^l$$
$$\times\left\{i!-\frac{\sqrt{\pi m}\cdot i\cdot(2i-1)!!}{2^i}\right\}. \qquad (9,\ I)$$

The approximate sum (9, I) is very close to the geometric progression with the denominator

$$q=\frac{12B^2}{m(\nu-\nu_0)^2}\cdot\left[1-\frac{\sqrt{\pi m}}{2}\right].$$

Noting that q, in the very worst case, does not exceed 0.3–0.35, we replace the sum (9, I) of the infinite, decreasing, geometric progression with the denominator indicated above. Then

$$K(\nu-\nu_0)\simeq\frac{\pi^{-1}\cdot\alpha\cdot\delta}{(\nu-\nu_0)^2}\cdot\frac{1}{1-\frac{12B^2}{m(\nu-\nu_0)^2}\cdot\left[1-\frac{\sqrt{\pi m}}{2}\right]}. \qquad (10,\ I)$$

From this expression it is possible to determine at what minimum distance from the center of the band ν_0 formula (7, I) is valid. If it is considered that the experimental determination of the absorption coefficient has a probable error of the order of 5–10%, then it follows that $q \approx 0.05 - 1$; after the simplest calculation we get:

$$\nu_{\min.}-\nu_0\simeq\pm\frac{11\div15B}{\sqrt{m}}\cdot\sqrt{1-\frac{\sqrt{\pi m}}{2}}. \qquad (11,\ I)$$

For example, for any of the bands of CO_2 formula (7, I) is valid at a distance $\nu_{\min} - \nu_0 \approx \pm$ 100–135 cm^{-1} from the center of the band; for the bands of CO $\nu_{\min} - \nu_0 \approx \pm$ 220–300 cm^{-1}. In practice in many cases $\sqrt{\pi m}/2 \ll 1$, as a result of which formulas (9, I), (10, I), and (11, I) are simplified.

An analogous examination of the absorption bands of spherical tops without a calculation of the influence of the Q branch (which it is possible to consider in first approximation as the line $n = 0$ is of anomalously large intensity) was carried out in the approximation that, for customary temperatures,

$$\alpha_n=\frac{m\sqrt{m}}{2\pi}\alpha\cdot(2n+1)^3\cdot e^{-mn(n+1)}. \qquad (2a,\ I)$$

For this condition the absorption coefficient for spherical tops assumes the following series:

$$K(\nu-\nu_0)=\sum_{n=-\infty}^{n=+\infty}\frac{\frac{m}{2}\cdot\sqrt{\frac{m}{\pi^3}}\cdot\alpha\cdot\delta\cdot(2|n|+1)^3\cdot e^{-m|n|\cdot(|n|+1)}}{(\nu-\nu_0+2Bn)^2+\delta^2}. \qquad (4a,\ I)$$

It is possible to show that at sufficiently large values of the argument $\nu - \nu_0$

$$K(\nu-\nu_0)\simeq\frac{\pi^{-1}\cdot\alpha\cdot\delta}{(\nu-\nu_0)^2}\cdot\frac{1}{1-\frac{18B^2}{m(\nu-\nu_0)^2}}. \qquad (10a,\ I)$$

Formula (7, I) is applicable at the distance (from the center of the band)

$$\nu_{\min.}-\nu_0\simeq\pm\frac{13.4\div19B}{\sqrt{m}} \qquad (11a,\ I)$$

Conditions (11, I) and (11a, I) partly overlap. Practically, it is possible to consider them as almost identical. For example, for any of the bands of CH_4 ($B = 5.24\ cm^{-1}$; $m = 256 \times 10^{-4}$ at $T = 300°K$), $\nu_{\min} - \nu_0 \approx \pm 435$–$620\ cm^{-1}$.

LIMITS OF THE ROTATIONAL STRUCTURE

Let us determine the very shortest distance from the center of the band at which formulas (9, I) and (10, I) are still realistic. It is also possible to define this distance as the largest for which it is still possible to note the rotational structure of the band. Actually, in the spectra of vibration-rotation bands of gases obtained using apparatus of high resolving power, it is possible to note that at the defined distance from the center of the band there is noted a sufficiently sharp transition from the line ("periodic") structure to the smooth, continuously decreasing curve. From this it is possible to draw the conclusion that on both sides of the center of any absorption band there exist sufficiently narrow frequency intervals, which appear like "limits of the rotational structure,"* since beyond these intervals the rotational

*In future we will use this term without quotation marks.

absorption maxima are not seen on the background of the wings of the central lines of the band; in the direction from the limits to the center the rotational structure of the absorption curve becomes notable and therefore can be discovered experimentally.

Introducing the coefficient ϕ, equal to the ratio of the magnitude of the background from the wings of the central lines (formulas (9, I) or (10, I)) to the magnitude of the rotational maximum for the corresponding frequency, and setting a necessary magnitude of this coefficient, it is possible to determine analytically the position of the limits of the rotational structure.

The magnitude of the rotational maximum of the nth line on the edge of the band is approximately

$$K_{\max.\ n}(\nu)\simeq\frac{\pi^{-1}\cdot\alpha_0\cdot\delta\cdot2p\,|n|\cdot e^{-mp^2n^2}}{\delta^2}.$$

The magnitude of the background is defined by formulas (9, I) or (10, I). Considering that the denominator of the geometric progression q cannot exceed 0.3–0.35, since in the opposite instance the asymptotic approximation (9, I) will give a significant error, we put the sum over N in (9, I) in the region of the limits of the rotational structure equal to the infinite geometric progression with the denominator $q = 1/3$, i.e., equal to 1.5. From the following computation it is possible to see that the magnitude of the sum depends only slightly on the final result.

We introduce a new interval, $y = \nu - \nu_0/B$, and symbol $g = \delta/B$. Taking into account that $y = 2pn$ and $\alpha_0 = pm\alpha/2$, we can write (considering only the positive values of y)

$$\frac{\pi^{-1}\cdot\alpha\cdot\delta}{B^2\cdot g^2}\cdot1.5=\varphi\cdot\frac{\pi^{-1}\cdot\alpha\cdot m\cdot p^2}{2B^2\cdot g^2}\cdot y\cdot e^{-\frac{my^2}{4}}.$$

Performing the necessary cancellations and taking

the logarithm of both parts of the equation, we finally have

$$0.108my^2 = 3\lg y + \lg\frac{mpp}{3g^2}. \qquad (12, I)$$

It is possible to solve Eq. (12, I) graphically for specific values of ϕ, m, p, and g. It can also be solved to a sufficient approximation for practice if log y is replaced by an interpolated Lagrange polynomial, constructed from three values of the argument y. Since the roots of Eq. (12, I) lie in the range $10 < y \leqslant 200$, we take for the indicated points $y_0 = 10$, $y_1 = 100$, and $y_2 = 200$. In this case, in the place of (12, I) we get a quadratic equation, from which it follows that

$$y_{\text{lim.}} = \frac{118}{540m + 0.63} + \sqrt{\frac{13924}{(540m + 0.63)^2} + \frac{2540 + 1000\lg\frac{mpp}{3g^2}}{108m + 0.126}}. \qquad (13, I)$$

of the rotational structure. The number of rotational lines in the absorption bands, which is determined experimentally using spectrometers of high resolving power, can be either approximately equal to, or several fewer than the number of lines in the lower lines of Tables 1 and 2, for the particular half-width of these lines. Indeed, the experimental data for the rotational structure of the bands of HCl [3] and of CO_2 [4, 5] are in excellent agreement with the calculated data.

Table 1. The Number of Rotational Lines in the Absorption Bands of CO_2 Within the Limits of the Rotational Structure (B = 0.39 cm^{-1}, p = 2, T = 300°K)

$\frac{1}{\nu}$	ϕ			
	2.0	1.0	0.25	0.10
0.075	81	85	95	99
0.125	71	77	85	93

Table 2. The Number of Rotational Lines in the Absorption Bands of HCl Within the Limits of the Rotational Structure (B = 10.34 cm^{-1}, p = 1, T = 300°K)

$\frac{1}{\nu}$	ϕ		
	2.0	1.0	0.25
0.005	25	29	33
0.125	21	25	27

Taking account of the minor dependence of the position of the limits of the rotational structure on the half-width of the rotational lines (i.e., on the external conditions), it is possible for an approximate calculation of the position of the limits to use the relation

$$\frac{12B^2}{m(\nu_{\text{lim.}} - \nu_0)^2} \approx \frac{1}{3},$$

from which

$$\nu_{\text{lim.}} - \nu_0 \approx \pm\frac{6B}{\sqrt{m}}. \qquad (14, I)$$

For example, for any of the bands of CO_2 from formula (14, I), we get $\nu_{\text{lim}} - \nu_0 \approx \pm 55$ cm^{-1}; for the bands of CO, $\nu_{\text{lim}} - \nu_0 \approx \pm 120$ cm^{-1}.

For the absorption bands of spherical tops, the position of the limits of the rotational structure can be approximately defined by the formula

$$\nu_{\text{lim.}} - \nu_0 \approx \frac{7.35B}{\sqrt{m}}. \qquad (14a, I)$$

For example, for any of the bands of methane, $\nu_{\text{lim}} - \nu_0 \approx \pm 250$ cm^{-1}; therefore, in absorption bands of methane (for the usual conditions) it is possible to observe experimentally no more than 45-47 rotational lines.

THE ABSORPTION COEFFICIENT WITHIN THE BOUNDS OF THE ROTATIONAL STRUCTURE

As already pointed out above, series (4, I) in the general case does not yield to an analytical summation. Accordingly, a numerical calculation of the series for a specific absorption band, typical for the group of molecules considered, was carried out. This characteristic band was taken to be the 4.26μ absorption band of CO_2 for T = 300°K and for four values of the ratio δ/B(0.10, 0.25, 1.0, 2.0). The summation was computed for all integral values of the argument

$$y = \frac{\nu - \nu_0}{B}$$

in the limits $-150 \leqslant y \leqslant +150$.

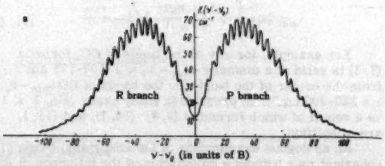
In Tables 1 and 2 are shown the numbers of rotational lines in the absorption bands of CO_2 and HCl within limits of the rotational structure, calculated on the basis of formula (13, I). The results are shown for two values of ϕ (200 and 8) and four values of g (0.10, 0.25, 1.0, 2.0). The data in the tables testify to the stability of the limits.

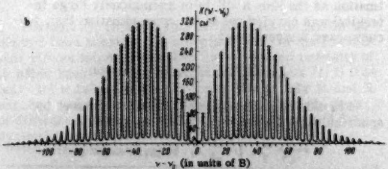
In the figure are presented graphically (by the solid lines) the results of the summation for two values of δ [0.1 cm^{-1} (0.25B) and 0.8 cm^{-1} (2B)].

For the purpose of the simplification of further calculations it was assumed that in the frequency interval ± pB from the center of each nth rotational line (with the intensity a_n) the absorption coefficient of the band approximately coincides with the absorption coefficient of the infinite succession of identical equidistant lines, each with the intensity a_n, and with the distance between the lines equal to 2 pB.

If the stated assumption appeared reasonable, then in the regions of each rotational line separately it was possible to use the formula of Elsasser,[1] which in the given case takes the form

$$K_n(\nu) = \frac{a_n}{2pB} \cdot \frac{\operatorname{sh}\frac{\pi\delta}{Bp}}{\operatorname{ch}\frac{\pi\delta}{Bp} - \cos\frac{\pi\nu}{Bp}}. \qquad (15, I)$$





Dependence of the absorption coefficient $K(\nu - \nu_0)$ for the 4.3μ band of CO_2 on $(\nu - \nu_0)$ for $\delta = 0.8$ cm^{-1} (a), and for $\delta = 0.1$ cm^{-1} (b). Solid line from formula (4, I); dotted line from formula (15, I).

The calculation, the results of which are presented graphically in the figure (dashed lines), show that for this application of Elsasser's formula the error of the determination of the absorption coefficient with its aid in the range $-100 \leqslant y \leqslant +100$ is extremely small (from 1-2% to 4-5% in the dependence on the half-width of the rotational lines). Beyond this frequency interval and up to the limits of the rotational structure (approximately, to $y \approx 150$-160), the error of formula (15, I) increases significantly, attaining at the very limit a quantity of the order of several tenths of a per cent (for small values of the ratio δ/B) and of one hundred per cent (for large values of the ratio δ/B), with the magnitude of the absorption coefficient appearing low.

As a consequence of the fact that for normal temperatures and pressures the half-width of the rotational lines δ of the absorption bands of CO_2 (and of many other gases) is significantly less than the rotational constant B (e.g., for the 4.26μ band of atmospheric CO_2 in the measurements of Adel, $\delta \approx 0.12$ cm^{-1}), formula (15, I) can be applied with confidence within the bounds of the entire rotational structure of the bands. Taking into consideration that the structure of infrared absorption bands of the group of molecules considered is of the same type, the analogous application of Elsasser's formula for all of the absorption bands examined is permissible.

REFERENCES

1. W. Elsasser. Heat Transfer by Infrared Radiation in the Atmosphere. 1942.
2. J. N. Howard, D. E. Burch, D. Williams. J. Opt. Soc. Am., 46, 186, 237, 334, 452 (1956).
3. E. Imes. Astrophys. J. 50, 251 (1919).
4. L. Kaplam. J. Chem. Phys. 18, 186 (1950).
5. P. Martin, E. Barker. Phys. Rev., 41, 291 (1932).
6. A. Adel. Phys. Rev. 90, 1024 (1953).

LAWS OF THE ABSORPTION OF INFRARED RADIATION IN THIN LAYERS OF SOME GASES II. ABSORPTION OF RADIATION IN THE VIBRATION-ROTATION BANDS OF SOME GASES

P. I. Bresler

Received 19 March 1959

Formulas are obtained connecting the intensity of radiation absorbed by a relatively thin layer of a gas, with the parameters of the particular vibration-rotation band of the gas. The limits of the application of the laws of the linear and of the quadratic roots of the absorption are determined.

The absorption of radiation in a gas layer in the limits of an infinitely narrow frequency interval from ν to $\nu + d\nu$ is defined by the Lambert-Beer law

$$J_\nu \cdot d\nu = J_{0_\nu} \cdot e^{-K(\nu)cl} \cdot d\nu, \qquad (1, II)$$

where J_{0_ν} is the intensity of the radiation incident on the absorbing gas and normal to the boundary of the layer, J_ν is the intensity of the radiation emerging from the layer of the absorbing gas of equivalent thickness cl,*

*The equivalent thickness is taken to be the product of the concentration of the absorbing gas and the particular thickness of the layer l in the mixture of the absorbing gas in nonabsorbing diluent for normal temperatures and pressures.

and $K(\nu)$ is the absorption coefficient.

In the following it is assumed that the radiation beam is parallel. The absorption of a nonparallel beam is equivalent in many cases to the absorption of a parallel beam in a gas layer of great thickness.

A parallel beam of radiation A, absorbed in a layer of gas of thickness cl, is defined by the following expression:

$$A = \int J_{0_\nu} \cdot [1 - e^{-K(\nu)cl}]\, d\nu. \qquad (2, II)$$

The limits of integration are dependent on the spectral characteristics of the incident beam and on the position and width of the particular absorption band.

For small cl within the limits of the absorption band (taking $J_{0_\nu} = J_{\nu_0} = \text{const.}$, where ν_0 is the center of the band) we get

$$A \cong J_{\nu_0} \alpha \cdot cl, \qquad (3, II)$$

where $\alpha = \int K(\nu) d\nu$ is the integrated intensity of the band.

For values of cl which are not large, significant absorption occurs only within the limits of the rotational structure; therefore, in the calculation of the absorbed radiation within the band limit, the absorption in the wings will not be included. In the preceding part (I), it was shown that for the vibration-rotation absorption bands of diatomic molecules of linear nonsymmetric, and also of linear symmetric, molecules with forbidden, odd, rotational levels (of the CO_2 type) the formulas of Elsasser (2) can be assumed to be applicable if they are used for each of the rotational lines separately.

If the "absorption function" of Elsasser, having the form

$$\frac{A_n}{J_{0_n} 2Bp} \cong \Phi\left[\frac{(\pi \cdot \alpha_n cl)^{1/2}}{2Bp}\right], \qquad (4, II)$$

is applied to each line of the rotational structure within the frequency limits $\pm pB$, reckoned from its center ν_{0_n}, where J_{0_n} is the intensity of the radiation incident on the gas layer in the frequency interval of the particular nth line, 2Bp is the distance between the centers of two neighboring lines (B is the rotational constant of the molecule, p = 1 for diatomic and linear nonsymmetric molecules, p = 2 for linear symmetric molecules with forbidden, odd rotational levels), δ is the half-width of the band, α_n is the integrated intensity of the nth line, and $\Phi(Z)$ is the probability integral, then the magnitude of the absorption in the band of the beam of radiation A is shown to be equal approximately to

$$A \cong \sum_{n=-\frac{3}{p}\sqrt{\frac{\pi}{\ln 2}}}^{n=+\frac{3}{p}\sqrt{\frac{\pi}{\ln 2}}} A_n \cong 2Bp \cdot J_{\nu_0} \cdot \sum_{n=-\frac{3}{p}\sqrt{\frac{\pi}{\ln 2}}}^{n=+\frac{3}{p}\sqrt{\frac{\pi}{\ln 2}}} \Phi\left[\frac{(\pi \alpha_n cl)^{1/2}}{2Bp}\right]. \qquad (5, II)$$

The intensity of the radiation incident on the gas layer can be taken as constant within the limits of the band and equal to J_{ν_0}. The limits of the summation are chosen on the basis of formula (14, I)* with

$$m = \frac{Bhc}{kT}\ [^1].$$

*The Roman numeral I in the formula numbers refers to the formulas of the first part of the present work.[1]

Let us substitute (without introducing a substantial error) the sum over n in (5, II) by an integral with the limits of integration ±∞. Then, taking account of the even character of the integrand, we get

$$A \cong 4Bp \cdot J_{\nu_0} \cdot \int_0^\infty \Phi\left[\frac{\sqrt{\pi} \cdot a_0 bcl}{2Bp} \cdot \sqrt{2pz+1} \cdot e^{-\frac{\pi}{2}pz(pz+1)}\right] dz,$$

where a_0 is taken from formula (2, I).

After simple calculations it is possible to write

$$A \cong 4Bp \cdot J_{\nu_0} \cdot \int_{\frac{1}{2p}}^\infty \Phi\left[\frac{\sqrt{\pi} \cdot a_0 bcl}{B \cdot \sqrt{2p}} \cdot e^{\frac{\pi}{4}} \cdot \sqrt{y} \cdot e^{-\frac{\pi}{2}p^2y^2}\right] dy.$$

The argument of the probability integral makes its contribution negligible since $e^{-y^2} \approx 1$. The lower limit of the integration can be equated to zero, with a resulting error significantly less than 1%.

For the calculation of the integral it is possible to use the solution of the probability integral in the power series

$$\Phi(z) = \frac{2}{\sqrt{\pi}} \cdot \sum_{k=1}^{\infty} (-1)^{k+1} \cdot \frac{z^{2k-1}}{(2k-1)(k-1)!} \qquad (6, II)$$

and carry out the resulting integration.

The final expression for the absorption of the radiation beam has the form

$$A \cong \frac{4.1 \cdot J_{\nu_0} \cdot \sqrt{abcl}}{\sqrt{p} \cdot \sqrt[4]{m}} \cdot \sum_{k=1}^{\infty} \frac{(-1)^{k+1} \cdot \left[\frac{\pi a \sqrt{m}\, bcl}{4B^2p}\right]^{k-1} \cdot \Gamma\left(\frac{2k+1}{4}\right)}{2.05 \cdot (2k-1)(k-1)!\left(k-\frac{1}{2}\right)^{\frac{k}{2}+\frac{1}{4}}}. \qquad (7, II)$$

Series (7, II) appears absolutely converging; however, for large values of cl its convergence is rather slow.

The maximum value of cl, for which formula (7, II) is still valid, can be determined from the condition of the negligibly small absorption in the wings of the band. An analytical determination of the absorption in the wings of the band presents great difficulty, since it is necessary to know and take into account the distribution function of the intensity in the radiation source. However, for the calculation of weak absorption in the wings, it can be assumed that the intensity of the radiation source is constant and equal to J_{ν_0}. In this case, the radiation beam A′, absorbed in the wings of the band of the molecule considered, is approximately equal to

$$A' \cong J_{\nu_0} \cdot \left[\int_0^{\nu_0 - \frac{0.2}{\sqrt{m}}} (1 - e^{-K(\nu-\nu_0)bl})\, d\nu + \int_{\nu_0+\frac{0.2}{\sqrt{m}}}^{\infty} (1 - e^{-K(\nu-\nu_0)bl})\, d\nu\right]$$

The limits of integration are taken to correspond with formula (14, I).

Taking, with some reservation,[1] that

$$K(\nu - \nu_0) \cong \frac{1.5 \cdot \pi^{-1} a^2}{(\nu - \nu_0)^2},$$

and integrating, we obtain

$$A' \cong J_{\nu_0} \cdot \frac{\pi^{-1} \cdot ab\sqrt{m}\, cl}{2B}. \qquad (8, II)$$

The relative magnitude A′/A of the beam absorbed in the wings to that absorbed in the central part of the band approximately equals

$$\frac{A'}{A} \cong \frac{0.04 \cdot \sqrt[4]{m^3} \cdot \sqrt{pabcl}}{\sum_{k=1}^{\infty} \frac{(-1)^{k+1} \cdot \left[\frac{\pi ab\sqrt{m}\, cl}{4B^2p}\right]^{k-1} \cdot \Gamma\left(\frac{2k+1}{4}\right)}{2.05 \cdot (2k-1)(k-1)!\left(k-\frac{1}{2}\right)^{\frac{k}{2}+\frac{1}{4}}}}. \qquad (9, II)$$

The sum of a descending alternating-sign series is always less than the first term (in the present instance, unity). For the determination of the order of magnitude of the thickness of the gas layer cl, for which formula (7, II) is still valid, we assume that the sum in the denominator of (8, II) for $(cl)_{max}$ equals 0.4 (with possible reservations). Assuming also that the ratio A′/A is equal to the probable relative error of measurement of the radiation beam, i.e., that A′/A ≈ 0.05-0.1, we have

$$(cl)_{max} \cong \frac{1 \div 4}{4ab\sqrt{pm}}. \qquad (10, II)$$

For example, for the 4.26μ band of CO_2 (α = 2700 cm^{-2},[3] δ = 0.12 cm^{-1} (in the atmosphere),[4] p = 2, B = 0.39 cm^{-1}, m = 19 × 10^{-4} for T = 300°K) $(cl)_{max}$ ≈ 4.7-18.8 cm.

Now let us examine the conditions of applicability of the law of the quadratic root

$$A \cong \frac{4.1 \cdot J_{\nu_0} \cdot \sqrt{abcl}}{\sqrt{p} \cdot \sqrt[4]{m}}, \qquad (11, II)$$

resulting from the first term of series (7, II). The relative error of the summation of this series is numerically equal to the magnitude of the first of the discarded terms. If the relative error of observation of formula (11, II) is taken equal to 0.1, then

$$(cl)^{\surd}_{max} \cong \frac{1.46B^2p}{ab\sqrt{m}}. \qquad (12, II)$$

The index √ indicates that condition (12, II) relates to the law of the quadratic root.

The lower limit of the applicability of the law of the quadratic root (11, II) can be found from the condition of the transition of this law into the law of linear absorption.

Elsasser's formula (4, II) is generally not applicable for very small values of cl as a result of the conditional assumptions used in its derivation. For very small values of cl, the absorption in the neighborhood of each line is defined by the linear law, and the total absorption corresponds to formula (3, II). For an increase in cl, the absorption of the central lines of the band begins to obey (4, II) while the absorption of the neighboring lines, having significantly lower intensities, still remains linear. Formula (11, II) becomes applicable when the absorption of the majority of the lines of the band obey formula (4, II) and it is possible to neglect the linear absorption of the outer lines. Hence, between the linear absorption law (3, II) and the law of the quadratic root (11, II) is located a transition zone.

An approximate analytical determination of the absorption in the range of the transition zone is possible, but hardly expedient, since all of the linear part of the absorption curve (including the transition region) appears rather narrow in the majority of cases. Practically, it is possible to consider that the transition from the linear absorption law to the law of the quadratic root occurs at an intersection point of functions (3, II) and

(11, II). From this we get the smallest value of cl, for which the law of the quadratic root is correct,

$$(cl)_{min}^{\surd} \cong \frac{16.8\delta}{a \cdot p \cdot \sqrt{m}}. \qquad (13, II)$$

For example, for the 4.26μ band of CO_2, $(cl)_{min}^{\surd} \approx 0.009$ cm, $(cl)_{max}^{\surd} \approx 0.03$ cm; for the 4.7μ band of CO ($a \approx 300$ cm^{-2},[5] $\delta = 0.065$ cm^{-1},[6] $B = 1.93$ cm^{-1}, $p = 1$, $m = 94 \times 10^{-4}$ for T = 300°K) $(cl)_{min} \approx 0.039$ cm, $(cl)_{max} \approx 3.0$ cm.

The analogous problem of the absorption of radiation can be solved also for the bands of spherical top molecules, if it is assumed that Elsasser's formula (4, II) can be applied to the separate lines of these bands, and if the absorption in the Q branch is not considered. For these conditions

$$A \cong \frac{4.25 \cdot \sqrt{abcl}}{\sqrt[4]{m}} \cdot J_{\nu_0} \cdot \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{(2k-1)^{k+1}} \cdot \left[\sqrt{\pi m} \cdot \frac{abcl}{B^2}\right]^{k-1}. \qquad (7a, II)$$

If, as formerly, we take the relative error of observation of the law of the quadratic root

$$A \cong \frac{4.25 \cdot J_{\nu_0} \cdot \sqrt{abcl}}{\sqrt[4]{m}}, \qquad (11a, II)$$

equal to 0.1, then the outside limit of applicability of this law is proved to be equal to

$$(cl)_{max}^{\surd} \cong \frac{1.52B^2}{ab\sqrt{m}}. \qquad (12a, II)$$

From the lower limit of applicability of the law of the quadratic root

$$(cl)_{min}^{\surd} \cong \frac{18\delta}{a \cdot \sqrt{m}}. \qquad (13a, II)$$

For example, for the 3.31μ fundamental band of CH_4 ($B = 5.24$ cm^{-1}, $a \approx 300$ cm^{-2},[3] $\delta \approx 0.10$ cm^{-1}, $m = 256 \times 10^{-4}$ for T = 300°K) $(cl)_{min} \approx 0.037$ cm, $(cl)_{max} \approx 8.7$ cm.

It is possible to show that, for the very same assumptions used earlier, for bands of linear symmetric molecules with an alternation of the statistical weights of the rotational levels

$$A \cong S \cdot \frac{4.1 \cdot J_{\nu_0} \cdot \sqrt{abcl}}{\sqrt[4]{m}}, \qquad (11b, II)$$

in which

$$S = \frac{\sqrt{f}+1}{\sqrt{2} \cdot \sqrt{f+1}},$$

where f is the ratio of the statistical weights of two adjacent rotational levels. For f = 1, S = 1; for f = 1/3, S = 0.985. Thus, the coefficient S, even for a significant difference of the statistical weights of adjacent rotational levels, differs only slightly from unity.

As already pointed out, the calculation of the influence of the Q branch has not been carried out by us; however, it is evident that this calculation can only lead to a change of the numerical coefficient in the formula of the law of the quadratic root.

The results obtained in Parts I and II can be used particularly for the investigation and calculation of infrared nondispersive instruments, among these being optical-acoustical gas analyzers, for which such an application allows by far the simplest means to compare the derived formulas with experiment. Some results of the investigation of optical-acoustical gas analyzers will be stated in the next part.

REFERENCES

1. P. I. Bresler. Opt. i Spektr. 7, 608 (1959).
2. W. Elsasser. "Heat Transfer by Infrared Radiation in the Atmosphere," 1942.
3. A Thorndike. J. Chem. Phys. 15, 868 (1947).
4. A. Adel. Phys. Rev. 90, 1024 (1953).
5. S. S. Penner and D. Weber. J. Chem. Phys. 19, 807 (1951).
6. D. Weber and S. S. Penner. J. Chem. Phys. 21, 1503 (1953).

THE ABSORPTION SPECTRUM OF LIQUID AND SOLID OXYGEN UNDER PRESSURE (12,600-3000 A)

V. I. Dianov-Klokov

Received 17 April 1959

Measurements were made of the intensity of the absorption spectrum of condensed oxygen at T = 86°K and at densities from $\rho = 1.16$ gm/cm^3 to $\rho = 1.6$ gm/cm^3 (pressures up to 8000 atm). It was found that the dependence of the absorption intensity on ρ is not the same for different groups of bands and is always high; for example, for wavelength 6290 A, $\varepsilon_m \sim \rho^{4.9}$ in the region of the existence of a liquid phase. From the curve $\varepsilon_m = f(\rho)$, an estimate was made of the change in volume for the transition, liquid – γ and $\gamma - \beta$.

INTRODUCTION AND PRESENTATION OF THE PROBLEM

The absorption spectrum of condensed oxygen in the region 12,600-3000 A, depending on the interaction of molecules, has been studied in all the states of aggregation of oxygen: solid[1-3] (α-, β-, γ-phases), liquid (including some mixtures)[4-6], and gaseous at medium[7-9] and high[10-13] pressures. The investigation of the temperature dependence of the intensity and the form of the band in compressed oxygen[10, 14] and a study of the dependence of the spectrum on temperature at constant volume[15] showed the definite influence of density on spectrum intensity.

In the present work an attempt has been made to determine directly the influence of oxygen density on the intensity of the spectrum in question at constant temperature, with the aim to discover the connection between the spectrum of condensed oxygen and its structure.

EXPERIMENTAL PART: METHOD

In the study of the dependence of the intensity of the band absorption in condensed oxygen as a function of the

density ρ, we made use of cuvettes similar to the ones described previously,[15] but without the needle valves. The change in volume of the working space was accomplished by the movement of a piston* with a Teflon and copper collar in the compression with an uncompensated area. For each experiment a new set of compression collars, having the form of a truncated cone, was used. The diameter of the smallest of the collars (resembling a mushroom) was made 0.2 mm larger than the cylindrical part of the canal (ϕ = 6.21 mm). (Tr. note: I believe this refers to the trunk shape of the mushroom.) The piston when assembled was tightly forced into the turning cone in such a way that the mushroom exerted pressure on its very end. After this the cuvette was placed in the spectrophotometer; its space was pumped out and connected by means of a drain tube to a Dewar flask filled with liquid oxygen. The excess gas pressure in the space was 200-400 mm Hg stp. After pouring liquid nitrogen into the outer jacket, the piston was forced into the canal for 2-3 mm, after which oxygen began to liquefy within the space; after a period of 15-20 minutes (for establishment of thermal equilibrium) the photometric study of the spectrum was begun.

*By means of a screw.

The procedure described above made certain that there would be a reproducible compression by the piston and sufficient purity (99-98%) of oxygen in the space, regardless of the various temperature coefficients of expansion of the materials in the compression collar and the cuvette.

To increase the strength of the optical windows made of fused quartz for pressures up to 8000 atm,* their lateral surfaces and faces were polished and all traces of the buffing were removed. The direct contact of the window with metal parts was prevented by the use of a Teflon gasket 0.05 mm thick (Fig. 1). The arrangement for connecting the window with the closing arrangement was kept the same as in the previously used cuvette.[15] Photometric spectral analysis for various positions of the piston was carried out with the help of a phase spectrophotometer,[16] which was provided with three energy sources: a photomultiplier P-3, a photoelement TS-G-4, and a photoresistance FS-A1. A series of 30-60 photometric spectrograms required on the average 2.5-3.5 hours. The last photographs, corresponding to the highest pressures, were repeated by moving the piston in the opposite direction to check for the absence of leaks. The temperature in the interior was determined for the initial spectrogram (without pressure) and for a layer of known thickness (12.75 and 5.3 mm) on the basis of (previous) data.[15] The beginning of the compression was determined by a break in the curve for the dependence of $\varepsilon_m = f(\rho)$ on the location of the piston. The calculation of the change in volume did not take into account any deformation of the cuvette or of the piston.

*The pressure in the cuvette was determined only at transition points for the extrapolation of the P-T diagram of the state of the solid phase of oxygen[18] and for the melting curve.[17] On the basis given in reference 20 it was also assumed to be essentially hydrostatic even after the freezing of the oxygen.

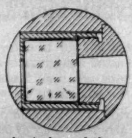


Fig. 1. Internal window of the cuvette (arrows indicate Teflon gaskets).

RESULTS

Figure 2 shows the dependence on ρ (T = 86°K) of the maximum absorption coefficient $\varepsilon_m = (1/l_{11}) \log_{10} (J_0/J)$ for all spectral wavelengths investigated; (Tr. note: l_{11} is layer thickness); Fig. 3 shows the spectrograms obtained. For the band head of group III* at 6290 A in the region of the existence of the liquid phase, $\varepsilon_m \sim \rho^{4.6}$, which is close to the results obtained from measurements at various temperatures[15] ($\varepsilon_m \sim \rho^{4.7}$). From the graph it can be seen that the rate of increase of ε_m with increasing ρ is different for different bands. Thus, in the case where T is variable and ρ is constant,[15] in each of the groups, the bands with the steepest dependence correspond to the electronic-oscillation transitions: 10,600 A—in group I; 5325 and 5769 A—in group III; 3612 and 3825 A—in group V. The electronic transitions without oscillation correspond to less sensitive internal groups: 12,600, 6290, and 3808 A, respectively. In agreement with the fact that in liquid oxygen about 40% of the intensity of the 7640 A band is associated with "independent" transitions within O_2 molecules, its intensity depends much less on ρ than is true in the other bands. These facts agree with our assumptions concerning the origin of the band spectra, that they are associated with the complex $(O_2)_2$, which interacts closely with its neighbors.[15] The graph of $\varepsilon_m = f(T)_{\rho = const.}$, however, differs from the graph of $\varepsilon_m = f(\rho)_{T = const.}$, because in the first case the curve is steeper, corresponding to the "unsymmetrical" groups I, II, and IV; and in the second case to

*For the classification see reference 15. Because the displacement of bands does not occur, their wavelengths are known for the spectrum of liquid oxygen.

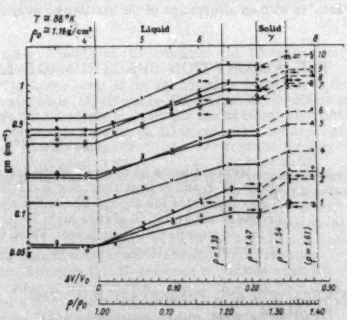


Fig. 2. Dependence of the extinction coefficient at band maximum on the density ρ of oxygen (the displacement of the piston in arbitrary units is plotted along the abscissa; the arrows indicate points obtained by reversing the direction of motion of the piston). Wavelengths (in A): 1—7640, 2—3285, 3—5325, 4—3808, 5—4773, 6—3612, 7—10,600, 8—12,600, 9—6290, 10—5769.

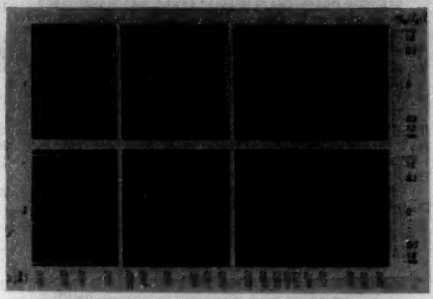


Fig. 3. Absorption spectra of condensed oxygen for varying densities (T = 86°K, path length = 5.3 mm). Density (in gm/cm³): 1—1.16; 2—1.61. The scales of the photographs along the wavelength axes vary somewhat for accidental reasons.

the "symmetrical" groups III and V. Apparently, this is associated with the fact that with increasing ρ the orientation of the molecules plays a more important role, and the assumption concerning the disturbing influence of the vessel, as in the analogous thermal disturbance, becomes invalid.

From Fig. 3 it is obvious that increasing the density of oxygen leads to an increase in the sharpness of the red end of the absorption band, noticeable even with the low resolving power (~80 cm^{-1}) of the spectrophotometer used. An analogous change in the appearance of the band at the transition from liquid to γ- and β-oxygen was observed by Prikhot' and his co-workers.[1] One can think of these phenomena as associated with the restriction of rotational and twisting oscillations of oxygen molecules in the lattice with increasing density.

The observed increase in intensity of spectrum with increasing ρ should not be considered only as the increase in the effective number of mutually compensating spins,* the number of which in liquid oxygen, according to Lewis' equation, at 86°K is equal to about 38% of the total amount.[19] From Fig. 2 it is obvious that the spectral intensity* increases approximately 2.5 times to the moment of freezing and continues to increase with further compression.* If one takes into account that the magnetic susceptibility of liquid and γ-oxygen are exceedingly small,[22] then the essential nature of the disturbance in the spectral intensity becomes clear.

*Concentration of diamagnetic "dimers" in Lewis terminology.

*With the exception of the 7640 A band, about which more will be said later.

*Because the recorded width of the band does not change materially, it is possible to approximate the calculation of the measured value ε_m for the proportional integral absorption.

From Fig. 2 it is possible to make a rough estimate of the change in molar volume of oxygen for the transitions liquid $\rightarrow \gamma$ and $\gamma \rightarrow \beta$ for T = 86°K:

$\Delta V_{l \rightarrow \gamma} \cong 1.25$ cm³ (P = 3000 atm; dP/dT = 127 atm/deg; cf. ref. 17)

and

$\Delta V_{\gamma\beta} > 1$ cm³ (P ≅ 8000 atm; dP/dT ≅ 180 atm/deg; extrapolation of data from ref. 16).

The corresponding heats of transition under the designated conditions proved to be in agreement with the Clausius Clapeyron equation, $\Delta H_{l\gamma} \cong 330$ kcal/mole, $\Delta H_{\gamma\beta} > 350$ kcal/mole. Although in the cuvette used the movement of the piston proved to be insufficient to cause complete transition, from the lower limit of $\Delta V_{\gamma\beta}$ it can be seen that the change in volume is sufficiently large (~5%). As a result it is possible to think, that the β- and α-phases of oxygen, obtained by cooling the γ-modification at atmospheric pressure, which are turbid and resemble "coarsely ground glass,"[21] are the result of the disintegration of particles into a fine powder. In the consideration of such an assumption, one could say that in our case the transition $\gamma \rightarrow \beta$ under pressure is not accompanied by a layer of turbidity.* Because in the calculation of the change in volume no account was taken of the deformation of the cuvette, the values of the density of oxygen quoted in Fig. 2, as a rough estimate, are high by 1-2%. Nevertheless, it is possible to conclude, with some confidence, that at T = 86°K, the density of γ- and β-oxygen, in accordance with the above considerations, is appreciably higher than at atmospheric pressure and is correspondingly greater at lower temperatures.

*This does not exclude the possibility that measurement of the magnetic susceptibility of β- and α-oxygen, formed after the application of pressure, leads to smaller values of χ than is ordinarily the case.

I wish to express my thanks to I. V. Obreimova for his interest in this work and for his helpful instruction; to A. I. Kitaigorodskovo and Ch. K. Mukhtarova for valuable discussions; to L. D. Lifshits for advice on the construction of the high pressure cuvette; and to D. D. Brezhneva, V. I. Lantsova, and R. V. Rumyantsevu for help in preparation of the apparatus and for carrying out the measurements.

REFERENCES

1. A. F. Prikhot'ko, M. Ruemann, and A. S. Fedoritenko. Zhur. Eksp. i Teoret. Fiz. 5, 712 (1935); Soviet Phys.—JETP 7, 410 (1935).
2. A. F. Prikhot'ko and M. Ruemann. Zhur. Eksp. i Teoret. Fiz. 5, 942 (1935); Soviet Phys.—JETP 8, 298 (1935).
3. A. F. Prikhot'ko. Zhur. Eksp. i Teoret. Fiz. 7, 929 (1937).
4. R. Guillen. Compt. rend. acad. sci. 198, 1223, 1486 (1934); Ann. phys. 8, 555 (1937).
5. V. I. Dianov-Klokov. Doklady Akad. Nauk SSSR 105,

290, 504 (1955); Opt. i Spektr. 1, 650, 862 (1956).
6. C. W. Cho, E. J. Allin, and H. L. Welsh. J. Chem. Phys. 25, 371 (1956).
7. W. Finkelnburg and W. Steiner. Z. Phys. 79, 69 (1932).
8. H. Salow and W. Steine. Z. Physik 99, 137 (1936); Nature 134, 463 (1934).
9. J. A. A. Ketelaar. Nuovo cimento 2, Suppl. No. 3, 763 (1955).
10. J. Robin. Compt. rend. acad. sci. 246, 1530 (1958).
11. J. Robin and S. Robin. Compt. rend. acad. sci. 236, 2393 (1953).
12. J. Robin and S. Robin. Compt. rend. acad. sci. 235, 792 (1953).
13. J. Robin and S. Robin. J. phys. radium 15, 331 (1954).
14. J. Robin, M. Desmaret, and F. Ubelmann. Compt. rend. acad. sci. 243, 1750 (1956).
15. V. I. Dianov-Klokov. Opt. i Spektr. 6, 457 (1959).
16. R. Stevenson. J. Chem. Phys. 27, 673 (1957).
17. R. L. Mills and E. R. Grilly. Phys. Rev. 199, 480 (1955).
18. V. I. Dianov-Klokov. Pribory i tekh. eksp. No. 2, 45 (1959).
19. V. I. Dianov-Klokov. Opt. i Spektr. 4, 448 (1958).
20. J. W. Stewart. Phys. Rev. 97, 578 (1955).
21. A. F. Prikhot'ko and A. A. Yavnel'. Zhur. Eksp. i Teoret. Fiz. 9, 789 (1939).
22. A. S. Borovik-Romanov, M. P. Orlova, and P. G. Strelkov. Doklady Akad. Nauk SSSR 99, 699 (1954).

THE LONG WAVELENGTH INFRARED SPECTRUM OF H_2O VAPOR AND THE ABSORPTION SPECTRUM OF ATMOSPHERIC AIR IN THE REGION 20-2500μ (500-4cm^{-1})

N. G. Yaroslavsky and A. E. Stanevich

Received 24 March 1958

The long wavelength infrared (rotational) spectrum of H_2O vapor in the region below 2500μ is discussed, as is the presence in the spectrum of an absorption band at 1634μ(6.12 cm^{-1}), corresponding to the rotational transition $2_2 - 3_{-2}$.

Quantitative data are obtained concerning atmospheric room air in the region 20-2500μ (500-4cm^{-1}) for a layer of air of thickness 10 meters at a temperature of 20°C, pressure of 760 mm of mercury, and absolute humidity of 10.5gm/m^3.

INTRODUCTION

The infrared, purely rotational, spectrum of H_2O vapor has been studied repeatedly. It has been subjected to the most detailed scrutiny in the region 18-135μ by Randall and others,[1] and in the region 45-1400μ in our preceding work.[2,3] In this spectral region, with the aid of the previously developed long wavelength infrared vacuum spectrometer DIKS-1,[4,5] about 100 rotational absorption bands of H_2O were recorded and interpreted, of which 34 bands had been previously observed.

At the present time, because of the use in the DIKS-1 spectroscope of a supplementary echelette with constant D = 5mm, and of a new source of long wavelength radiation, the spectral operating band of the instrument has been broadened, bringing about the possibility of conducting various spectral researches in a very wide interval of the long wavelength infrared spectrum—from 20 to 2500μ. In particular, there have been added to the results of research on the long wavelength infrared spectrum of H_2O[2] data recorded in the regions from 20 to 45μ and from 1400 to 2500μ.

In agreement with the calculations of Benedict and his colleagues,[6] the presence of an absorption band at about 1630μ, corresponding to the rotational transition $2_2 - 3_{-2}$, should be expected as the significance of rotational terms of the H_2O molecule. This band, actually, was observed by King and Gordy in the neighborhood of 1628μ, but only with the use of the methods of microwave radiospectroscopy, and not in the infrared absorption spectrum of water vapor, which up to the present time has been studied exactly and in detail only in the region of wavelengths below 1500μ.[2,6]

In the present article the results of study of the rotational spectrum of the H_2O molecule in the wavelength range from 1400 to 2500μ are presented, and also data received in the study of the transparency of atmospheric room air in the region of the spectrum from 20 to 2500μ.

As is known, the transparency of atmospheric air in the infrared region of the spectrum, and in particular, in the wavelength range from 18 to 2500μ, is chiefly defined by the absorption of water vapor in the air. In the longer wavelength region, absorption occasioned by the oxygen of the air takes place, the corresponding absorption bands of O_2 being located at about 2500μ (a weak band) and about 5000μ (a strong band).[7*]

*At the still longer wavelengths (microwave) of the spectrum near 13,500μ (13.5mm), a strong absorption band is observed, belonging to atmospheric water vapor and corresponding to the rotational transition $5_1 - 6_{-1}$.[7]

It should be noted that some information about the transparency of the atmosphere in the long wavelength infrared region of the spectrum is given by the theoretical work of Van Vleck.[10,11] Teissing and Caplan[12] refined these data, having measured the attenuation of solar radiation by atmospheric water vapor by means of filters and thermal detectors in the region 900-3600μ. Only qualitative data about the transparency of the atmosphere in the region below 1500μ are presented in the works of Genzel[8] and Gebbie.[13,14] However, sufficiently exact quantitative data concerning the absorption of infrared radiation by atmospheric air in the region of the spectrum from 20 to 2500μ are not available in the literature.

EXPERIMENTAL METHOD

To embrace the entire spectral interval from 20 to 2500μ in the DIKS-1 instrument, six echelettes are used in the first order, each 270 × 270 mm in size. Three echelettes were engraved with respectively 12, 6, and 2 lines per millimeter on a precision ruling engine in the laboratory of F. M. Gerasimov. The remaining three echelettes, with constants 1.5, 2.5, and 5.0 mm, and blaze angle about 10 deg, were prepared on an ordinary milling machine.

The sources of long wavelength radiation were: an electrically incandescent platinum ribbon at a temperature of 1200°C, covered with yttrium oxide* (for the region of the spectrum from 20 to 50μ), and a PRK-4 mercury lamp (for the region from 50 to 2500μ). The receiver of the spectrally distributed radiation was an optico-acoustical receiver, supplied with hermetic chambers with windows of cesium iodide and crystal quartz.

*The results of the study of this source are given in reference 15.

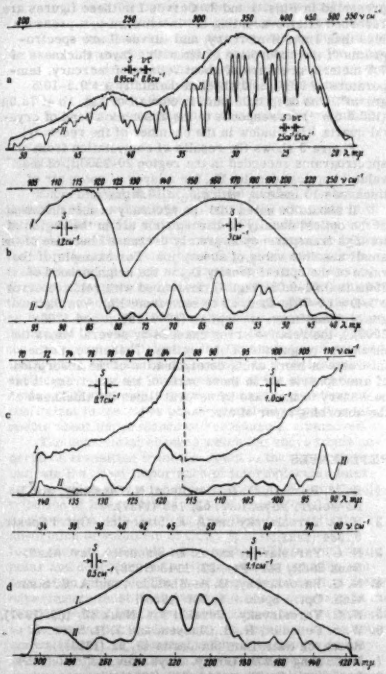


Fig. 1. Spectrograms of absorption in the region 20-300μ for atmospheric air in a layer of thickness 7.5 meters, at a temperature of 20°C, pressure of 760mm of mercury, and absolute humidity of 9.5-10 gm/m³.

Radiation sources: a—yttrium oxide covered platinum ribbon at a temperature of 1200°C; b,c,d—PRK-4 mercury lamp. Echelette constants D (in mm); a—0.083; b,c—0.167; d—0.5. Slit width S (in mm): a—1.5; b,c—5; d—6. Time constants τ (in sec): a—10; b,c—30; d—100. Echelette-filter constants d_1 and d_2 (in mm): a—0.04; b,c—0.02 and 0.04; d—0.3. Supplementary filters: a—1mm polyethylene + soot; d—1mm crystal quartz + soot. Amplification (in arbitrary units): a—3; b,c—2; d—8.

The spectra were recorded automatically with the aid of an electronic potentiometer EPP-09, connected to the output stage of the main electronic amplifier. Depending upon the region of the spectrum being recorded and the necessary value of the signal-to-noise ratio, the spectrum scanning speeds v and receiver-recording system time constants τ are chosen to be such as to insure the necessary precision of measurement of wave numbers ν and transmission T. The average error in the measurement of the wave number $\Delta\nu$ was 0.02cm^{-1}, and the error in determination of the transmission ΔT had limiting values from 3 to 5%. For example, in recording the rotational spectrum of H_2O vapor in the region from 1000 to 2500μ (Fig. 2c), v and τ had limiting values equal respectively to 0.03 cm^{-1}/min and 200 sec. The signal-to-noise ratio was equal to 50, and the conditions of precision of measurement of ν and T were fulfilled.

The exclusion of the energy of spectra of higher order and of diffusion of short wavelength radiation was accomplished by means of compensated selective modu-

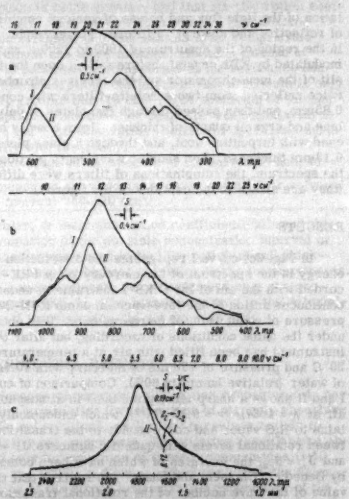


Fig. 2. Spectrograms of absorption in the region 300-2500μ for atmospheric air in a layer of thickness 7.5 meters at a temperature of 20°C, pressure of 760mm of mercury, and absolute humidity of 10.5 gm/m³.

Radiation sources—PRK-4 mercury lamp. Echelette constants D (in mm): a—1.5; b—2.5; c—5. Slit width S (in mm): a,b,c—1. Time constant τ (in sec): a,b—100; c—200. Echelette-filter constants d_1 and d_2 (in mm): a—0.5 and 0.5; b,c—0.85 and 0.85. Supplementary filters: a,b—1mm polyethylene + soot; 1mm crystal quarts + soot; c—the same + 0.13 glass. Amplification (in arbitrary units): a—7; b—12; c—16.

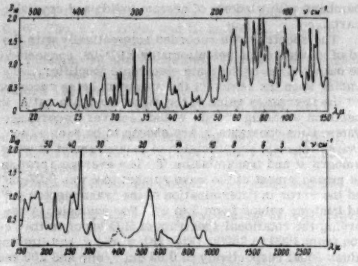


Fig. 3. Optical density of atmospheric (room) air in the region 20-2500μ, for a layer of thickness 10 meters at a temperature of 20°C, pressure of 760mm of mercury, and absolute humidity of 10.5 gm/m³.

lation of the light flux and by use of various combinations of reflective and absorptive filters. For example, in work in the region of the spectrum of 1000 to 2500μ, radiation modulated by KBr crystal, before falling upon the input slit of the monochromator and the receiver chamber, was twice reflected from two echelette-filters with constant 0.85mm, and then passed through two plates of polyethylene and crystal quartz of thickness 1mm heavily blackened with turpentine soot, and through a glass plate of 0.13mm thickness. For shorter wavelength portions of the spectrum, the combinations of filters were different (they are shown in the captions of the figures).

RESULTS

In Fig. 2c, curve I represents the distribution of energy in the spectrum of the mercury lamp PRK-4, recorded with the aid of the DIKS-1 instrument, under continuous action of the fore-vacuum pump RVN-20 to a pressure of about 1mm of mercury; curve II is obtained under the same conditions of recording, but after the instrument has been filled with air at a temperature of 20°C and pressure of 760mm of mercury with 10.5gm/m³ of water (relative humidity 60%). Comparison of curves I and II shows a sharp absorption band in atmospheric air at $\lambda = 1634\mu$ ($\nu = 6.12$ cm^{-1}), which undoubtedly pertains to H_2O vapor and corresponds to the transition between rotational levels with quantum numbers $J''_\tau = 2_2$ and $J'_\tau = 3_{-2}$, the energies of which have been computed by Benedict, Classen, and Shaw.[6] We remark that the value of the wave number of the rotational transition $2_2 \rightarrow 3_{-2}$ (6.12 cm^{-1}) obtained by us in the long wavelength infrared absorption spectrum of H_2O vapor is within the limits of error of measurement (0.02 cm^{-1}) in accordance with the value of frequency of this transition, 6.14 cm^{-1} (1628μ), defined by the method of microwave radiospectroscopy.[7]

The results of the study of the absorption of atmospheric (room) air over a wide range of the long wavelength infrared spectrum extending from 20 to 2500μ are

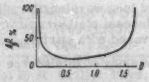


Fig. 4. A curve of the relative error in the determination of optical density of atmospheric (room) air.

presented in Figs. 1 and 2. Curves I in these figures are recorded after evacuating the instrument to a pressure less than 1mm of mercury, and curves II are spectrograms of the absorption of air with a layer thickness of 7.5 meters, pressure of about 760mm of mercury, temperature of 20°C, and absolute humidity ρ = 9.5-10.5 gm/m³. The deep minimum in curve I of Fig. 1b at 78.5μ (125.5 cm^{-1}) corresponds to the absorption band of crystal quartz (the window in the chamber of the receiver).

Figure 3 shows the results of computation from all spectrograms recorded in the region 20-2500μ, of the value of optical density D_{10} for a layer of room air of thickness 10 meters, with ρ_{H_2O} = 10.5 gm/m³.

It should be noted that the accuracy of measurement of the optical density of atmospheric air in the region of its high transparency is greatly decreased because of the small absolute value of absorption. For example, if the value of the optical density D_{10} in the neighborhood of 350μ is 0.04-0.05 (Fig. 3), measured with relative error $\Delta D/D$ = 60-70%, then, as is seen from Fig. 4 in the regions of minimum absorption (1200-1500μ and 1700-2500μ), the relative error exceeds by several times the measured magnitude of absorption. Therefore, in the interests of more exact determination of the absorption of atmospheric air in these parts of the spectrum, it is necessary to increase by several times the thickness of the absorbing layer of air.

REFERENCES

1. H. M. Randall, D. M. Dennison, N. Ginsburg, and L. R. Weber. Phys. Rev. 52, 160 (1937).
2. N. G. Yaroslavsky and A. E. Stanevich. Opt. i Spektr. 5, 384 (1958).
3. N. G. Yaroslavsky and A. E. Stanevich. Izv. Akad. Nauk SSSR, Ser. Fiz. 22, 1145 (1958).
4. N. G. Yaroslavsky, B. A. Zheludov, and A. E. Stanevich. Opt. i Spektr. 1, 507 (1956).
5. N. G. Yaroslavsky. Uspekhi Fiz. Nauk 62, 159 (1957).
6. W. S. Benedict, H. H. Classen, and J. H. Shaw. J. Research Natl. Bur. Standards 49, 91 (1952).
7. W. S. King and W. Gordy. Phys. Rev. 93, 407 (1954).
8. L. Genzel. Z. Phys. 144, 311 (1956).
9. J. O. Artman. Phys. Rev. 96, 1237 (1954).
10. J. H. Van Vleck. Phys. Rev. 71, 413, 425 (1947).
11. J. H. Van Vleck and W. S. Weisskopf. Rev. Mod. Phys. 17, 227 (1945).
12. H. H. Teissing and P. J. Caplan. J. Appl. Phys. 27 518 (1956).
13. H. A. Gebbie. Phys. Rev. 107, 1194 (1957).
14. H. A. Gebbie. J. Phys. Radium 19, 230 (1958).
15. A. E. Stanevich and N. G. Yaroslavsky. Inzh. Fiz. Zhur. 1, 49 (1958).

INFLUENCE OF SOLVENT ON THE INTENSITIES OF RESONATING INTRAMOLECULAR VIBRATIONS OF CARBON TETRACHLORIDE

M. P. Lisitsa and L. A. Ovander

Received 10 March 1959

The most intense resonance doublet of carbon tetrachloride, corresponding to the vibrations $\nu_1 + \nu_4$ and ν_3, was investigated in solutions of different concentrations. The solvents used were benzene, toluene, dioxane, and methylacetate. In all cases, increase in the concentration of CCl_4 was accompanied by an increase in the intensities of the doublet components, and latter reaching their maximum values in pure carbon tetrachloride. The intensity of the vibration $\nu_1 + \nu_4$ increased much faster indicating an increase in the resonance interaction of the levels $E_{\nu_1+\nu_4}$ and E_{ν_3} when there was an increase in interaction between the CCl_4 molecules. The frequencies of the resonating vibrations and the magnitude of resonance splitting, depend on the concentration.

INTRODUCTION

Experimental results, obtained earlier,[1] on the intensities of the vibrations ν_3 and $\nu_1 + \nu_4$ occurring in the infrared absorption spectrum of CCl_4, indicated a considerable weakening in the resonance interaction between the vibrational levels E_{ν_3} and $E_{\nu_1+\nu_4}$ when the phase transition liquid-vapor occurred. However, resonance does not disappear completely, since within the limits of the experimental errors the splitting remained the same as before, although the intensity of the summation mode decreased by more than 4 times (if for the liquid phase the absorption coefficient at the band maximum reached 19000 cm^{-1}, then in the case of vapor, it decreased to 4000 cm^{-1}). For the first overtone of the summation mode which does not undergo resonance, the absorption coefficient in the vapor phase is still so large that all doubts about the presence of resonance are removed.

The substantial changes which the above bands undergo on transition from the liquid to the vapor state, indicate the great importance of intermolecular interactions which play a far from secondary role in the distribution of intensities of the above-mentioned bands. In connection with this it is expedient to investigate the absorption of solutions of CCl_4. It is desirable to perform such experiments with several different solvents, polar and nonpolar, and in the maximum possible concentration interval. The most important result of these experiments must be the expected sharp decrease in the intensity of the long wavelength component corresponding to the summation mode $\nu_1 + \nu_4$, on decrease in the concentration of CCl_4, determined by a weakening in the intermolecular interaction between the molecules of carbon tetrachloride. At the same time, it will become possible to clarify the relation between the magnitude of the resonance splitting and the solution concentration.

To solve the problem formulated above, the authors of this paper investigated the absorption of carbon tetrachloride in three polar and one nonpolar solvents.

It must be noted that the choice of solvent is very limited, since in the spectral region 740-820 cm^{-1}, the overwhelming majority of organic compounds absorb strongly. Of the substances available, the most suitable were benzene, toluene, dioxane, and methyl acetate. These substances are not completely transparent in the spectral region of interest to us, but their average absorption coefficients do not surpass 20-50 cm^{-1}. At the very beginning of the spectral region investigated, the absorption of dioxane was slightly larger than 10 cm^{-1}. Towards the end of the region it increases by about two times. The presence of two weak maxima does not hinder the performance of measurements or the calculation of results. The spectrum of methyl acetate differs from that of dioxane in that there are no maxima, that its absorption is twice greater, and that its absorption coefficient increases faster with frequency than dioxane. Of the four solvents, benzene has the most complicated spectrum; it has three maxima, the most intense of which is between the components of the resonance doublet. The absorption coefficient in that maximum is only slightly greater than 70 cm^{-1}. The spectrum of toluene is simpler. If one does not count the weak maximum at ν = 778 cm^{-1}, its absorption coefficient decreases monotonically with frequency.

Knowledge of the spectra of the solvents* and, in particular, of their absorption coefficients allowed the determination of the possible concentration interval of CCl_4, and in each case to find the optimum cell thicknesses giving the highest precision in the measurements.

*We measured the absorption curves of all four solvents in the interval 740-820 cm^{-1}.

All measurements were performed on a spectrophotometer IKS-11. The maximum error in the determination of transmission did not exceed 2-3%.

EXPERIMENTAL RESULTS

Because of numerous difficulties encountered in performing quantitative investigations of strongly absorbing liquids and solutions, we limited ourselves mainly to qualitative measurements. Quantitative results were obtained only for solutions of three concentrations (1:50, 1:100, and 1:200) in dioxane. They permitted the determination of the strong concentration dependence of the intensities of both doublet components; in particular, the intensity of the bands increases with increase in concentration. The rate of growth for the summation mode was found to be larger than for the fundamental mode.

The results of qualitative experiments are given in Tables 1-4. As an example, we also include one figure illustrating the absorption of solutions of CCl_4 in benzene. Analysis of the curves shows that increase in concentration is accompanied by strengthening of the resonance interaction between the vibrational levels, since the height of the long wavelength maximum corresponding to the summation mode $\nu_1 + \nu_4$ increases faster than the maximum of the short wavelength component. If for the minimum concentration the ratio of the intensities of the two maxima is about 2, then in the case of pure CCl_4 it is about 1, i.e., both absorption bands have comparable

intensities (the latter is characteristic of almost complete resonance).

Table 1 allows also a number of other conclusions to be drawn. The first thing that attracts attention is change in the position of the maxima on increase in concentration. In comparison with pure CCl_4, the maximum of the long wavelength component in the most dilute solution (1:25) is shifted by 3 cm^{-1} to higher frequencies, while the shift of the short wavelength maximum reaches 6 cm^{-1}; as a result, the splitting is increased by 3 cm^{-1}.

While increasing with increasing dilution, the frequencies of both vibrations do not attain the values characteristic of the isolated molecule. Thus, the effect of the interaction between the solvent molecules and the solute molecules partly compensates the interaction between like molecules. This compensation also becomes evident on comparison of the intensities of the doublet components of gaseous CCl_4 and the most dilute solutions: in the gaseous state, the ratio of the intensities is greater than 4, as was mentioned above, while in the most dilute solution the short wavelength component is not more than 2 to 3 times more intense than the long wavelength component.

It is possible to point at still another fact showing the analogy between the solution and pure CCl_4. It is known[1] that the weaker band of the doublet is split (in the case of the gas) into five components, as a result of isotopic shift. In the liquid state CCl_4 does not exhibit any such splitting, and it is also absent in the case of solutions.

Tables 2-4 make it clear that the polar solvents toluene, dioxane and methylacetate lead to completely analogous results. It is characteristic of the solutions studied that it is impossible to find a simple relation between change in vibration frequency and resonance splitting, on the one hand, and the magnitude of the dipole moment of the solvent molecule, on the other. Thus, for example, the shifts of the corresponding maxima are completely equal, whether benzene or toluene was used as solvent, although the benzene molecule does not possess a constant dipole moment.

In the second pair of solvents (dioxane and methylacetate) the shifts of the same maxima are greater. Notwithstanding the fact that the dipole moment of the methylacetate molecule is four times that of the dioxane molecule, the shift is practically the same in both cases.

From Tables 1-4 it can be seen that there exists complete parallelism between concentration and the magnitude of resonance splitting: within the limits of experimental error, the splitting is the same for equal concentrations in different solvents.

DISCUSSION

A number of particularities discovered during the course of our investigation of the resonance interaction between the vibration modes ν_3 and $\nu_1 + \nu_4$ of carbon tetrachloride in solution can not be explained in the absence of a rigorous theory. Nevertheless, the latter circumstance is not an obstacle to a qualitative discussion of some, if not all of the manifestations described above.

Let us first examine the shift of the absorption maxima of the resonance doublet components on transition from pure CCl_4 to solutions of various concentrations. As has been noted above, this shift is towards increased frequency of vibration and increases with decrease in concentration. This manifestation is quite ordinary. It is caused by a decrease in the interaction between like molecules and it must be emphasized that such a decrease is not compensated by interaction with the solvent molecules. Because of the presence of the solvent, the frequencies of the maxima, even in the case of the most dilute solutions, are found to be smaller than the corresponding frequencies for the gas. In order to correctly answer the question, why in all cases the frequency of the fundamental mode is the one affected most, it is necessary to know the magnitude of the shift of the maxima corresponding to the vibrations ν_1, ν_2, and ν_4 (or their combinations) during the phase transition

Table 1. Influence of Solvent (Benzene, Dipole Moment of the Molecule d = 0) on the Characteristics of the Resonance Doublet ν_3 and $\nu_1 + \nu_4$ of Carbon Tetrachloride

Concentration of solution	Ratio of intensities at the band maxima	$\nu_1+\nu_4$ (cm^{-1})	ν_3 (cm^{-1})	$\Delta(\nu_1+\nu_4)$ (cm^{-1})	$\Delta\nu_3$ (cm^{-1})	$\varkappa$ (cm^{-1})
1 : 25	1.98	785	790	3	6	25
1 : 15	1.70	785	788	3	5	24
1 : 10	1.48	785	788	3	5	24
1 : 5	1.38	785	788	3	5	24
1 : 2	1.30	785	788	3	5	24
1 : 1	1.25	784	787	2	3	23
1 : 0.50	1.19	784	787	2	3	23
1 : 0.25	1.15	784	787	2	3	23
Pure CCl_4	1.07	782	784	0	0	22

Table 2. Influence of Solvent (Toluene, Dipole Moment of the Molecule d = 0.37 D) on the Characteristics of the Resonance Doublet ν_3 and $\nu_1 + \nu_4$ of Carbon Tetrachloride

Concentration of solution	Ratio of intensities at the band maxima	$\nu_1+\nu_4$ (cm^{-1})	ν_3 (cm^{-1})	$\Delta(\nu_1+\nu_4)$ (cm^{-1})	$\Delta\nu_3$ (cm^{-1})	$\varkappa$ (cm^{-1})
1 : 50	1.87	785	789	3	5	24
1 : 25	1.76	785	789	3	5	24
1 : 15	1.60	785	789	3	5	24
1 : 10	1.53	785	789	3	5	24
1 : 5	1.47	785	789	3	5	24
1 : 1	1.42	784	788	2	4	24
1 : 0.5	1.39	784	787	2	3	23
1 : 0.25	1.28	784	787	2	3	23
Pure CCl_4	1.07	782	784	0	0	22

Table 3. Influence of Solvent (Dioxane, Dipole Moment of the Molecule d = 0.43 D) on the Characteristics of the Resonance Doublet ν_3 and $\nu_1 + \nu_4$ of Carbon Tetrachloride

Concentration of solution	Ratio of intensities at the band maxima	$\nu_1+\nu_4$ (cm^{-1})	ν_3 (cm^{-1})	$\Delta(\nu_1+\nu_4)$ (cm^{-1})	$\Delta\nu_3$ (cm^{-1})	$\varkappa$ (cm^{-1})
1 : 25	2.49	788	793	6	9	25
1 : 15	2.41	788	793	6	9	25
1 : 10	2.36	788	793	6	9	25
1 : 5	2.17	788	792	6	8	24
1 : 2	1.86	787	791	5	7	24
1 : 1	1.74	787	791	5	7	24
1 : 0.50	1.16	785	787	3	3	22
1 : 0.25	1.10	784	787	2	3	22
Pure CCl_4	1.07	782	784	0	0	22

Table 4. Influence of Solvent (Methylacetate, Dipole Moment of the Molecule d = 1.67 D) on the Characteristics of the Resonance Doublet ν_3 and $\nu_1 + \nu_4$ of Carbon Tetrachloride

Concentration of solution	Ratio of intensities at the band maxima	$\nu_1+\nu_4$ (cm^{-1})	ν_3 (cm^{-1})	$\Delta(\nu_1+\nu_4)$ (cm^{-1})	$\Delta\nu_3$ (cm^{-1})	$\varkappa$ (cm^{-1})
1 : 50	1.77	788	792	6	8	24
1 : 15	1.70	788	792	6	8	24
1 : 10	1.54	788	792	6	8	24
1 : 5	1.49	788	792	6	8	24
1 : 2	1.44	787	791	5	8	24
1 : 1	1.34	787	791	5	8	24
1 : 0.50	1.10	785	788	3	5	24
1 : 0.25	1.08	785	787	3	3	22
Pure CCl_4	1.07	782	784	0	0	22

liquid-vapor. Such data is available, unhappily, only for the vibration mode ν_3. Finally, let us note that shifts caused by resonance are part of the total shifts under examination. Since both modes have equal shifts due to resonance, and the directions of the latter are known, their presence does not introduce additional difficulties into the treatment of the present problem.

The magnitude of the full splitting x of the resonance doublet, which increases with decrease in concentration, is directly related to the shifts of the maxima. Although the total increase x does not exceed 3 cm^{-1}, i.e., is barely beyond the limit of experimental error (1-1.5 cm^{-1}), nevertheless the tendency towards increase is very clear in all four solvents (Tables 1-4). In the case of a gas,[2] the value of x can be calculated with the help of the formula

$$x = [\Delta^2 + 4(H_v^{v'})^2]^{1/2}, \qquad (1)$$

where Δ characterizes the difference in energy between the nonexcited levels E_{ν_3} and $E_{\nu_1+\nu_4}$,

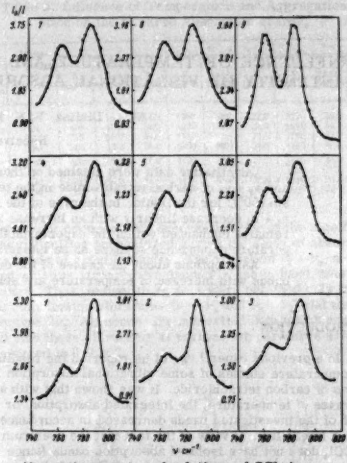
$$H_v^{v'} = \int \psi_v H \psi_{v'} d\tau$$

is the matrix elements of the energy of excitation related to the presence of resonance interaction, and v and v' are the vibration quantum numbers. The above relation can not be used for examination of the condensed state including solutions, without serious assumptions. However, if we assume that the form of the relation remains unchanged for the condensed state, then the increase in x, on solution, is apparently caused by change in both factors, i.e., in the magnitude of the natural splitting Δ and in the magnitude of the matrix element $H_v^{v'}$. The latter term must increase with increase in concentration, reaching its maximum magnitude for pure CCl_4. As has been pointed out above x must, at the same time, decrease until it reaches the value characteristic of the pure liquid and vapor. This means that Δ varies in the opposite direction, i.e., decreases, at a higher rate than $H_v^{v'}$ increases. The discussion given above is in complete accord with the experimentally discovered increase in the intensity of the long wavelength resonance doublet component with increase in CCl_4 concentration. Indeed, the transfer of energy from the fundamental mode to the summation mode must increase with decrease in natural splitting Δ (if, for example, the nonexcited vibrational levels coincide fully, i.e., $\Delta = 0$, then the intensities of the two doublet components will be equal) as well as with increase in magnitude of the matrix element $H_v^{v'}$.

It was shown[1] that in the case of gaseous CCl_4 the long wavelength component is split into several bands, due to the presence of two chlorine isotopes in molecules of carbon tetrachloride. In solution and in liquid CCl_4 no such splitting is observed. This is explained by the broadening of the separate absorption bands leading to complete overlap of each other, on transition from the gaseous state to the condensed state.

CONCLUSIONS

1. The resonance interaction between the vibrational levels E_{ν_3} and $E_{\nu_1+\nu_4}$ of carbon tetrachloride in solution



Absorption spectra of solutions of CCl_4 in benzene of varying concentrations. Concentrations: 1—1:25; 2—1:15; 3—1:10; 4—1:5; 5—1:2; 6—1:1; 7—1:0.5; 8—1:0.25; 9—pure CCl_4.

is stronger than in the gaseous state, but weaker than in the pure liquid.

2. It has been determined that resonance splitting is concentration dependent. With increase in concentration the magnitude of the splitting decreases, reaching its limiting value for liquid CCl_4.

3. The shift in the maxima of the resonance doublet components increases with decrease in the concentration of the solution, i.e., with increase in interaction between the solvent molecules and those of the solute.

4. Because of the broadening of the separate absorption bands on transition from the gaseous to the solution state, the isotopic structure of the vibration absorption band $\nu_1 + \nu_4$ disappears completely.

5. It was not found possible to determine the relations between the magnitude of the dipole moment of the solvent and the resonance splitting, on the one hand, and the change in the frequencies of the vibrations investigated, on the other.

REFERENCES

1. M. P. Lisitsa and V. N. Malinko, Opt. i Spektr. 4, 455 (1958).
2. M. V. Volkenshtein, M. A. Elyashevich, and B. I. Stepanov. "Vibrations of Molecules." State Publishing House for Technical and Theoretical Literature, Moscow-Leningrad, 1949.

INFLUENCE OF TEMPERATURE AND OF THE STATE OF AGGREGATION ON THE INTENSITY OF VIBRATIONAL ABSORPTION BANDS OF CARBON TETRABROMIDE

M. L. Lisitsa, V. N. Malinko, and I. N. Khalinmonova

Received 10 March 1959

Quantitative data were obtained on the intensities of intramolecular vibrations $2\nu_3$, $\nu_1 + \nu_3$, and $\nu_3 + \nu_4$ of carbon tetrabromide in the temperature range 30-90°C for the solid phase and 95-150°C for the liquid. In the case of the solid phase, the intensities of vibrations $2\nu_3$ and $\nu_1 + \nu_3$ decrease linearly with an increase in temperature while the intensity of vibration $\nu_3 + \nu_4$ remains unchanged within the experimental limits of error. In the case of liquid CBr_4, no temperature dependence of these same intensities was noticed.

Assumptions about the causes of the decrease of the integrated absorption of vibrational bands with increase of temperature are stated.

INTRODUCTION

In a previous paper,[1] two of us reported the results of temperature studies of some vibrational absorption bands of carbon tetrachloride. It was shown that with an increase of temperature, the integrated absorption for each of the investigated bands decreased in accordance with a linear law. In view of the fact that the spectrum of CCl_4 does not have isolated absorption bands (since many compound modes of various orders, including some investigated in reference 1, resonantly interact with each other), it is of interest to carry out a similar study of the spectra of a material which is structurally analogous to CCl_4 and which possesses isolated absorption bands. For this purpose we have chosen carbon tetrabromide; this molecule does not have Fermi interactions of vibrational levels and belongs to the same space group of T_d symmetry.

The infrared spectrum of CBr_4 has been studied only slightly. The most substantial results, in our opinion, were obtained by Plyler, Smith, and Aquista[2] who studied the absorption of solutions of carbon tetrabromide in CS_2 and CCl_4. Data about the absorption of pure CBr_4 are presented for the first time in the present paper.

MEASUREMENT METHODS

The method of quantitative studies of the infrared absorption of CBr_4 is not different in principle from that described earlier[3]; however, the physical-chemical properties of the given compound contribute to it certain peculiarities which must be checked.

In order to perform measurements in the liquid phase an absorption cell of the usual construction was employed. Through one of the windows were bored two openings, to which, with the help of glyptal, glass nipples were fastened. These were used for filling the cell with the substance being studied. The sides of the cell at the contact between the lead spacer and the windows were coated with a thin layer of glyptal. A measurement of thickness was made by the interference method after polymerizing the glyptal.

The cell was filled in the following manner. The glass nipples were filled with CBr_4 which had been ground to a powder, after which the system was slowly heated to the melting point of the powder. The resulting liquid flowed inwards, forming a continuous transparent layer between the windows. In order to avoid leakage and evaporation of the liquid during measurements, the nipples were sealed.

For every temperature studied a recording of the radiation passing through the cell was made no less than three times for an increase of temperature from the melting point, and as many times again for its fall from the highest temperature reached.

The influence of thermal radiation[4] on the absorbing layer was taken into account automatically, since the measurements were made from a pair of cells of different thicknesses. To a significant degree this permitted us to eliminate the influence of multiple reflections.

In order to obtain a sufficiently transparent crystalline layer the liquid contained in the cell was cooled slowly to the temperature of solidification and then to the freezing point. A single crystal was not obtained even during prolonged cooling; the sufficiently transparent film on the window was polycrystalline and possessed marked dispersion, which increased with a reduction of temperature (Fig. 1). The dispersion was especially significant in the region of substantial α-modification. Thus, true values of the absorption coefficient can be found only from a strict calculation of the dispersion effect.

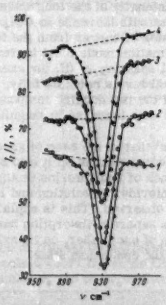


Fig. 1. Transmission of polycrystals of CBr_4 in the region of the bands which correspond to vibration $\nu_1 + \nu_3$. 1—30°C; 2—50°C; 3—70°C; 4—90°C.

As the basis for such calculations an assumption was made concerning the absence of absorption by the crystals in the spectral regions which are adjacent to the base of the bands. Such an assumption is justified in practice by the full transparency of the liquid phase in

those same spectral regions.* As a result of the above mentioned assumption, the dispersion radiation was excluded by the following means. For every temperature, a curve was constructed of the ratio of the intensities I_2' and I_1' of the radiation passing through layers of thicknesses d_2 and $d_1 (d_2 > d_1)$ both in the region of the absorption band and in the neighborhood of its base. The difference of the ratio I_2'/I_1' from unity in the region of transparency for the liquid phase is explained by dispersion. Passing a straight line through the points which correspond to transparent regions, it is easy to establish the requisite correction factor. If the value of light dispersion is calculated as independent of absorption,[5] which is wholly admissible for weak absorption bands, then the correction factor c has the form

$$c = I_2'/I_1'. \qquad (1)$$

In the general case, as follows for example from Fig. 1, the factor c is a function of wavelength. Thus, in the construction of a true absorption curve it is necessary to make use of the correction factor at every point. Taking this discussion into account, the final equation for calculating the absorption coefficient can be written in the form

$$k = \frac{1}{d_2 - d_1} \ln\left[c \cdot \frac{I_1}{I_2}\right], \qquad (2)$$

where I_1 and I_2 are the intensities of the radiation passing through the thin and thick layers in the absorption band (in the transparent region $I_1' = I_1$, $I_2' = I_2$, and $k = 0$). All the curves presented above for crystalline CBr_4 were constructed by the method described above.

The error in measuring the integrated absorption coefficient for liquid does not exceed 5-7%. The execution of additional operations connected with the dispersion calculation in a polycrystalline layer increased the latter by one and one-half. For both crystals and liquid each curve was the mean of no less than six recordings of the spectrum.

*The phase transition from liquid to solid insignificantly changes the position of the maxima of the investigated spectral bands.

MEASUREMENT RESULTS

In the detection of vibrational bands of pure CBr_4 in the liquid and solid states, we were guided by the qualitative data of Plyler et al.[3] relating to a solution of CBr_4 and CS_2 and CCl_4. As is seen from Table 1, the values of the frequencies for the liquid, determined in our experiments, are only slightly different from those for solutions which confirms the weak influence of the solvents used on the position of the maxima (in reference 2 a band was not cited with a maximum at 851 cm^{-1}; this is reliably identified by us as $\nu_3 + \nu_4$). All attempts to follow a temperature dependence for the intensity of the fundamental vibration ν_3 were not crowned with success in view of the significant difficulties encountered during the study of absorption bands of great intensity. The vibration $\nu_3 + \nu_3$, a band which is strongly overlapped by the ν_3 band, was not studied. Thus, temperature data were obtained only for two combination vibrations ($\nu_1 + \nu_3$ and $\nu_3 + \nu_4$) and the overtone $2\nu_3$. All necessary numerical data which characterize these vibrations at various temperatures are presented in Table 2.

Table 1. Frequency of Absorption Maxima of the Vibrational Bands of CBr_4

Vibration	ν_{max} (cm^{-1}) data of authors	ν_{max} (cm^{-1}) exp. data[3]
$\nu_3 + \nu_3$ . . .	790	787
$\nu_3 + \nu_4$ . . .	851	—
$\nu_1 + \nu_3$ . . .	932	934
$2\nu_3$	1332	1333

Table 2. Influence of Temperature and Aggregation State on the Infrared Absorption of CBr_4

State of aggregation	Vibration / t° C	$\nu_1+\nu_3$ s (cm^{-2})	$\nu_1+\nu_3$ k_{max} (cm^{-1})	$\nu_1+\nu_3$ r (cm^{-1})	$\nu_3+\nu_4$ s (cm^{-2})	$\nu_3+\nu_4$ k_{max} (cm^{-1})	$\nu_3+\nu_4$ r (cm^{-1})	$2\nu_3$ s (cm^{-2})	$2\nu_3$ k_{max} (cm^{-1})	$2\nu_3$ r (cm^{-1})
Crystal	30	410	16.5	23.5	1290	52.0	22.0	2270	58.0	32.0
	50	403	15.5	24.0	1200	49.5	23.0	1870	46.0	35.0
	70	397	15.0	24.5	1150	43.5	23.5	1585	37.0	40.0
	90	390	15.5	25.0	1090	38.0	24.0	1560	32.0	45.0
Liquid	93	405	15.5	27.0	1190	46.5	23.5	1840	35.0	45.0
	110	403	15.0	29.5	1200	49.0	23.0	1840	35.0	45.0
	130	400	14.5	31.0	1190	45.0	25.0	1880	37.0	48.5
	150	407	14.5	31.0	1180	44.0	26.0	1920	38.0	47.5

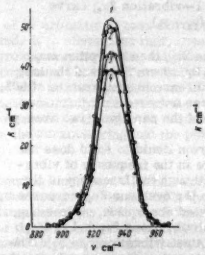


Fig. 2

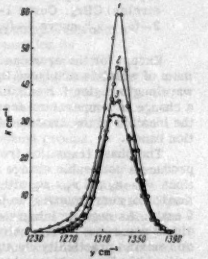


Fig. 3

Fig. 2. Absorption of crystalline CBr_4 in the region of the bands corresponding to vibration $\nu_3 + \nu_3$. Curve 1—30°C; curve 2—50°C; curve 3—70°C; curve 4—90°C.

Fig. 3. Absorption of crystalline CBr_4 in the region of the first overtone vibration $2\nu_3$. Curve 1—30°C; curve 2—50°C; curve 3—70°C; curve 4—90°C.

We shall examine the results of the temperature experiments. For the solid phase the corresponding curves are presented in Figs. 2 and 3. The character of the change in the integrated absorption and half-widths are shown in Figs. 4 and 5. From these data it follows that the most significant temperature dependence for a band is connected with the overtone $2\nu_3$ (Fig. 3), the integrated absorption of which sharply decreases while the half-width increases with an increase in temperature. For the combination band $\nu_1 + \nu_3$ these same characteristics vary in a smaller degree. These changes are not noticeable in the band corresponding to the vibration $\nu_3 + \nu_4$. Thus, stronger temperature dependence of the band intensity occurs for the highest frequency of vibrational transition. Such an effect does not occur, however, for the earlier investigated absorption bands of carbon tetrachloride.[5] Moreover, in spite of the significant difference of vibrational frequencies in the latter case, even the reverse dependence is found.

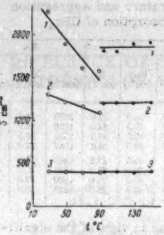


Fig. 4

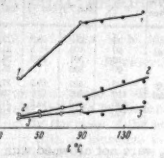


Fig. 5

Fig. 4. Temperature dependence of integrated absorption of various bands of crystalline (open circles) and liquid (solid circles) CBr_4. Curve 1—vibration $2\nu_3$; curve 2—$(\nu_1 + \nu_3)$; curve 3—$(\nu_3 + \nu_4)$.

Fig. 5. Temperature dependence of half-widths Γ of various bands of absorption of crystalline (open circles) and liquid (solid circles) CBr_4. Curve 1—vibration $2\nu_3$; curve 2—$(\nu_3 + \nu_4)$; curve 3—$(\nu_1 + \nu_3)$.

Except for the overtone $2\nu_3$, the absorption maximum of which is displaced by ~6 cm^{-1} toward the long wavelength region for an increase in temperature of 60°, a change in temperature does not have an influence on the location of the maxima of the remaining two absorption bands.

The phase transition from liquid to solid does not produce a noticeable change in the frequency of vibrations $\nu_3 + \nu_4$ and $\nu_1 + \nu_3$, although the frequency of the maximum corresponding to the overtone $2\nu_3$ increases by 5 cm^{-1}. As regards integrated absorption, on freezing, it either somewhat increases (vibrations $2\nu_3$ and $\nu_1 + \nu_3$), or remains practically constant (vibration $\nu_3 + \nu_4$). The half-width Γ remains unchanged on freezing only for the overtone $2\nu_3$. In the case of vibration $\nu_3 + \nu_4$, it increases somewhat; for vibration $\nu_1 + \nu_3$ it decreases very slightly. These variations in practice do not appear beyond the limits of error of the measurements; in this connection, evidently, it is possible to assume that the phase transition of liquid to solid is not accompanied by a change in Γ of the studied absorption bands.

Results of experiments on the temperature dependence for the liquid phase show the invariability (within the experimental limits of error) of the integrated intensities of all three bands (Fig. 4). It is true that an examination of the appropriate curves shows a small decrease in absorption at the maxima with an increase of temperature. However, the half-width Γ increased by approximately the same amount, which is clearly evident from the graphs presented in Fig. 5. The opposite direction of these factors explains the constancy of the integrated intensities S of the corresponding vibrations.

DISCUSSION

The results of the measurements carried out for crystalline CBr_4 lead to the conclusion that the qualitative temperature dependence of the studied absorption bands appears the same as in the case of certain bands of carbon tetrachloride,[1] i.e., with an increase of temperature the integrated intensity of the radiation absorption decreases in accordance with a linear law which can be represented in the form

$$S = S_0 + \alpha T, \tag{3}$$

where S is the integrated absorption at temperature T, S_0 is the integrated absorption when T = 0 for the crystalline phase or when T is the melting point in the case of the liquid phase, and

$$\alpha = \frac{dS}{dT} \leqslant 0.$$

It follows from our experiments that for liquid CBr_4, $\alpha = 0$. The temperature coefficient for the vibrational band $\nu_3 + \nu_4$ in the crystal is also zero. For the two remaining vibrations in the crystal, $\alpha \neq 0$ and is different.

Equation (3) does not provide for a change in S with pressure.* Actually, an increase in temperature can lead to an increase in pressure if the coefficient of volume expansion of the investigated substance significantly exceeds the coefficient of volume expansion of the material of the spacer, cell window, and seals or adhesives. This additional pressure can have an influence either on the contour of an absorption band or on its intensity. In connection with this, the change of integrated absorption in the temperature experiments can be more fully described by

$$S = S_0 + \left(\frac{\partial S}{\partial T}\right)_P \cdot T + \left(\frac{\partial S}{\partial P}\right)_T \cdot P. \tag{4}$$

The satisfactory agreement of the results of our experiments with Eq. (3) confirms a small change in pressure for the temperature used.

Thus, the few qualitative data on the temperature dependence of the intensity of the vibrational absorption bands of a substance in a condensed state led to one and the conclusion: the coefficient of integrated absorption decreases with an increase in temperature according to a linear law.

The established dependence differs in principle from that of the gaseous state where a rise in temperature is accompanied by a nonlinear growth of the integrated absorption.[6]

In the latter case, the temperature dependence is determined by one particular factor, namely, the population of energy levels of the molecule. This is well confirmed by theory and experiment.[7] For the solid and liquid phase this factor plays a significantly smaller role, since the measurements were carried out at a lower temperature and mostly at $kT \ll h\nu$. At temperatures close to room temperature, the factor $\exp(-h\nu/kT)$ can have a substantial influence only on vibrations whose frequencies are lower than 100 cm^{-1}. Thus, at comparatively low temperatures in the most accessible region of the infrared spectrum ($\lambda \leqslant 25\mu$) the temperature dependence under consideration is determined by some other factors. The most probable of these, in our opinion, are: (a) change of lattice parameters (crystal) or the average distance between molecules (liquid) and (b) change of the life time of the molecule in the equilibrium state, caused by a change in temperature.

Actually, if the factor $\exp(-h\nu/kT)$ plays a small role, then any temperature dependence of the intensity of an intramolecular vibration must be connected exclusively with a change of intermolecular interactions. An increase

*The decrease in the number of absorbing centers in the beam path caused by thermal expansion of CBr_4 was taken into account in the calculation of the absorption coefficient by the introduction of an appropriate correction.

of lattice constants or mean distance between neighboring molecules (in the liquid) leads to a decrease in the overlapping of electron clouds of the interacting molecules, i.e., to a decrease in the matrix elements of the interaction. The latter must appear in the form of a multiplicative factor in that part of the integrated absorption which is temperature dependent,* i.e., with an increase in temperature that part must decrease. A decrease of lifetime of the molecules in the equilibrium state caused by an increase of temperature leads to a similar effect. (In order to exclude the influence, in this case, of the effect described above, the mean distance between neighboring molecules should be considered fixed.)

*It is possible to calculate that the constant part of the integrated absorption corresponds to T = 0° (crystal).

REFERENCES

1. M. P. Lisitza and V. N. Malinko. Isv. Akad. Nauk USSR, Ser. Fiz. **22**, 1117 (1958).
2. E. K. Plyler, W. H. Smith, and N. Aquista. J. Res. Nat. Bur. Stand. **44**, 503 (1950).
3. M. P. Lisitza and V. N. Malinko. Opt. i Spektr. **4**, 455 (1958).
4. I. S. Khvashchevskaya. Thesis, Minsk, 1958.
5. M. Yasumi. Bull. Chem. Soc., Japan **28**, 489 (1955).
6. M. P. Lisitza and V. N. Malinko. Ukrainskii Fiz. Zhur. **3**, no. 6 (1958).
7. M. P. Lisitza and V. L. Strizhevskii. Opt. i Spektr. (in print).

SPECTRA OF ORGANO-BORON COMPOUNDS OF THE AROMATIC SERIES

A. N. Nikitina, V. A. Vaver, N. S. Fedotov, and B. M. Mikhailov

Received 13 April 1959

The electronic absorption spectra of solutions of 27 aromatic organo-boron compounds and the Raman spectrum of one of them were investigated. It is shown that light absorption by organo-boron compounds containing two aromatic groups surpasses the additive absorption of light by two aromatic groups and by organo-boron compounds with one aromatic group. The interaction between the boron and the aromatic groups was interpreted in terms of the electron-acceptor properties of the boron atom in these compounds. It is shown that the rather high absorption intensity for the bands near 230-240 mμ, observed in the spectra of phenyl-substituted borazoles, is determined by the interaction between the borazole ring and the phenyl groups.

At present there is a rather extensive literature on the investigation of vibrational spectra of organo-boron compounds. However, insofar as their electronic spectra are concerned, there are very few papers on this subject.[1,2]

The absorption spectra were measured on a spectrophotometer SF-4. Heptane was used as solvent. The integrated intensity coefficients of lines in the Raman spectrum were measured photographically for solutions in CCl_4. The unit of intensity was taken to be $1/100$ of the integrated intensity of the 313 cm^{-1} line of CCl_4 calculated for 1 mole. The spectrum was excited using the 4358 A line of mercury. The results obtained are given in Tables 1 and 2.

As can be seen from Table 1, the spectra of organo-boron compounds containing one phenyl group (Nos. 1 and 2) can be compared (in the long wavelength region) with the spectra of monosubstituted benzenes such as toluene and phenol. In the intensity of their absorption, they occupy a place intermediate between toluene and phenol. However, the presence of a sharp and intense absorption line around 235 mμ in the spectra of organo-boron compounds with one phenyl group substantially differentiates the latter from toluene and phenol.

In the absorption spectra of the majority of the organo-boron compounds with two phenyl groups investigated by us and also in that of triphenylboron (No. 11, Table 1), we observed two electronic transitions: one at 240-250 mμ, and the other, less intense, at about 270 mμ. Light absorption by organo-boron compounds with two phenyl groups surpasses considerably the additive absorption by two phenyl, tolyl groups or organo-boron compounds with one phenyl ring. This follows from the electronic absorption spectra as well as from the Raman spectrum. It is known that the intensity of the corresponding lines in the Raman spectrum are extremely sensitive to the mutual influence of atomic groups. The intensity of the 1600 cm^{-1} line (antisymmetric vibration of the benzene ring) strongly depends on the character and nature of the substituent, and can be used to evaluate the interaction between the substituent and the benzene ring.[3] It is seen from Table 2 that the integrated intensity of the 1600 cm^{-1} in the Raman spectrum of the isobutyl ester of diphenylboric acid is about five times greater than the intensity of this line in the spectra of compounds such as toluene, phenol, benzene, diphenylmethane, and is equal to the intensity of this line in the spectrum of diphenyl.

Introduction of the substituents CH_3 and Cl into the para positions of the phenyl rings of the organo-boron compounds (Nos. 4-6, Table 1), leads to the same effect as in the corresponding monosubstituted benzenes, i.e., a shift to the long wavelength side of the spectrum and an increase in absorption intensity.

The spectra of the organo-boron compounds with two naphthyl groups investigated by us exhibit two electronic transitions: one at 220 mμ and the other at 290-300 mμ, while for organo-boron compounds with a phenyl and naphthyl groups they appear at 240 mμ and 282.5 mμ (Table 1). Analogous to organo-boron compounds with two phenyl groups, the light absorption by the organo-boron compounds with two naphthyl groups also surpasses (although to a lesser extent) the additive absorption of two naphthyl groups. It must be noted that, relative to phenyl groups, the α-naphthyl groups cause greater steric hindrance in the molecules of organo-boron compounds. The spectra of the majority of organo-boron compounds with two α-naphthyl groups investigated by us are comparable, in their intensity and character of absorption, to the corresponding spectrum of α,α'-dinaphthyl (Table 1).

Table 1. Electronic Absorption Spectra of Solutions of Aromatic Organo-Boron Compounds

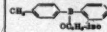
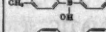
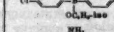
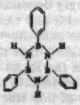
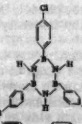
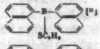
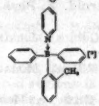
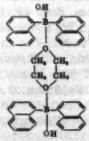
No.	Compound	λ_{max} (mμ)	ϵ_{max}	Compound	λ_{max} (mμ)	ϵ_{max}
1		220 235 255 260 267.5 275	86[a]) 2520 495 538 622 480		242.9 253.8 262 265.5 269.0	78.5 182.0 221.8 117 221.8
2		222.5 235 267.5 272.5 280	9000 6400 758 777 596		258.8 265.2 270.2 273.0 277.4	831.7 1858.0 1584.0 1560.0 2520.0
3		240 270	20500 1285		248	18820
4		250	23000		243 249 256 260 262 268.9 268.3	200 320 430 470 480 350 430
5		250	24250		255	20200
6		250 280—285	33050 2300—2500		280	21400
7		240 260—270	24100 2000—2200	—	—	—
8		240 272.5	18000 1100	—	—	—
9		240 260—270	17000 810	—	—	—
10		240 260—270	17800 1060	—	—	—
11		240 270	10850 2220	—	—	—
12		230 262.5—265	45000 950		248	38000
13		240 267.5	54700 1200	—	—	—
14		222.5 295—300	98800 14100		225 290	113000 17800
15		222.5 300	100000 14300		225 282 295	88200 14300 13200
16		220 300	84400 11400		245 310	78500 22400
17		222.5 295—300	92000 13700		220 ~280—290 ~320	100000 ~4000—5250 234 ~ 5250 234

Table 1 (cont'd)

No.	Compound	λ_{max} (mμ)	ϵ_{max}	Compound	λ_{max} (mμ)	ϵ_{max}
18		222.5 287.5	100000 15600	–	–	–
19		222.5 285—287.5	96000 13900	–	–	–
20		222.5 295—300	76900 11800	–	–	–
21		222.5 300	62000 8800	–	–	–
22		240 282.5	19350 8400	–	–	–
23		240 282.5	18750 8200	–	–	–
24		240 282.5	17800 7120	–	–	–
25		250—265	1800	–	–	–
26		265—280	4225	–	–	–
27		222 300	18000 4000	–	–	–

*Ethanol solutions were used.

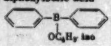
From the spectra examined by us, it follows that the boron atom in organo-boron compounds, interacts with the aromatic groups.

It is known[21] that the electronic spectra of poly- (and mono-) phenyl compounds with such central atoms as N, P, S (in particular N) exhibit, relative to the spectra of benzene or toluene, a shift towards the long wavelength side and a considerable increase in absorption intensity caused, according to the opinion of the authors, by the interaction between the unshared electron pair of the atoms N, P, S, and the π electrons of the phenyl rings. In contrast to nitrogen, the boron atom does not have an unshared electron pair. However, the interaction of boron with the aryl groups can be explained on the basis of the electron-acceptor properties of the boron atom determined by the presence of a vacant 2p level, as a result of which the boron atom attracts to itself the π-electron clouds of the aromatic groups.

The majority of the organo-boron compounds investigated by us were acids, esters, amines or thioesters, in whose molecules such electron donating groups as OH, OCH_3, OC_4H_9, NH_2, $N(C_2H_5)_2$, NC_4H_9, and SC_4H_9 are placed near the boron atom. Although the presence of these groups probably increases the absorption intensity in the spectra of the corresponding organo-boron compounds, this increase apparently does not have a decisive influence. Thus, for example, in the spectra of di-α-naphthyl boron chloride (No. 21, Table 1) and of phenyl-α-naphthyl boron chloride (No. 23, Table 1) a decrease is observed in the intensity of the absorption bands relative to the spectra of analogous compounds with electron donating groups. However, this lowering is not very substantial, particularly if one takes into consideration the circumstance that a certain decrease in intensity can be caused by an increase in steric hindrance resulting from introduction into the molecule of a chlorine atom instead of nitrogen or oxygen.

Furthermore, in the absorption of triphenylboron (No. 11, Table 1) the absorption band around 240 mμ is nearly twice weaker than the corresponding band in the spectrum of the isobutyl ester of diphenylboric acid (No. 3, Table 1), although the number of benzene rings is

Table 2. Integrated Intensity Coefficients (I_{co}) of the 1600 cm^{-1} line in the Raman Spectrum

No.	Compound	I_{co}
1	Isobutyl ester of diphenylboric acid 	700
2	Diphenyl	730 [19]
3	Phenol	40 [20]
4	Toluene	39 [20]
5	Benzene	35 [20]
6	Diphenylmethane	70

Note. The data on the intensity of the diphenylmethane spectrum was kindly provided by Z. B. Alaune, to whom the authors express their gratitude.

greater in the former compounds. Nevertheless, triphenylboron possesses a rather considerable absorption if one also takes into account the fact that, in its molecule, the planes of the phenyl rings are rotated relative to each other[22] to a larger extent than in the organoboron compounds with two phenyl groups investigated by us.

We also investigated the spectra of some complexes of organo-boron compounds of the aromatic series (Nos. 7, 24-27, Table 1) with ammonia, pyridine, or dioxane. It is difficult to interpret the absorption spectra of these complexes since they represent the manifestation of the influence of several factors, in particular, a different valence state of boron, the tetrahedral configuration of the molecule, and the semipolar nature of the bond.

The borazoles and their phenyl derivatives occupy a special place among the organo-boron compounds. We investigated the absorption spectra of B-tri(p-chlorphenyl)-borazole and B-triphenylborazole. The spectrum of the latter has been investigated earlier[1] but the authors did not measure the more intense short wavelength region of the spectrum, and as a result did not discover the absorption band about 230 mμ. This band, and also the more intense band shifted to 240 mμ (under the influence of the chlorine atoms in the para position) in the spectrum of B-tri(p-chlorphenyl)borazole, are quite intense thus indicating the interaction between the phenyl rings and the borazole ring. The 230 mμ in the spectrum of B-triphenylborazole can be compared, to a certain extent, with the corresponding band in the spectrum of 1,3,5-triphenylbenzene, although the latter is more intense and shifted towards the long wavelength side of the spectrum. However, it is known[23, 24] that in the far ultraviolet the absorption spectra of borazole and benzene are alike, but the spectrum of benzene is more intense and slightly shifted to the long wavelength region. Hence, the spectra of the phenyl-substituted borazoles investigated by us can serve as further substantiation for the contention that, in the excited state, the electronic structure of borazole is similar to that of benzene.

REFERENCES

1. H. J. Becher and S. Frick. Z. Phys. Chem. **B12**, 241 (1957).
2. M. J. S. Dewar, V. P. Kubba and R. Pettit. J. Chem. Soc. 3073, 3077 (1958).
3. B. M. Mikhailov and V. A. Vaver. Doklady Akad. Nauk SSSR **102**, 53 (1955).
4. B. M. Mikhailov and V. A. Vaver. Izv. Akad. Nauk SSSR, Ser. Khim. **20**, 451 (1956).
5. B. M. Mikhailov and V. A. Vaver. Izv. Akad. Nauk SSSR, Ser. Khim. **21**, 812 (1947).
6. B. M. Mikhailov and V. A. Vaver. Izv. Akad. Nauk SSSR, Ser. Khim. **22**, 419 (1956).
7. B. M. Mikhailov and V. A. Vaver. Zhur. Obshchei Khim. **29**, 2248 (1959).
8. B. M. Mikhailov and N. S. Fedotov, Izv. Akad. Nauk, Ser. Khim. **20**, 375 (1956).
9. B. M. Mikhailov and T. V. Kostroma. Zhur. Obshchei Khim. **29**, 1477 (1959).
10. B. M. Mikhailov and N. S. Fedotov. Zhur. Obshchei Khim. **29**, 2244 (1959).
11. B. M. Mikhailov, T. K. Kozminskaya, N. S. Fedotov, and V. A. Dorokhov. Doklady Akad. Nauk SSSR **127**, 1023 (1959).
12. K. L. Wolf and W. Herold. Z. Phys. Chem. **B13**, 201 (1931).
13. M. Pestemer and O. Gübitz. Monatsch. Chem. **64**, 426 (1934).
14. M. Pestemer and L. Wiligut. Monatsch. Chem. **66**, 119 (1935).
15. W. R. Orndorf, R. C. Gibbs, A. McNulty, and C. V. Shapiro. J. Amer. Chem. Soc. **49**, 1541 (1927).
16. M. T. O'Shaugnessy and W. H. Rodebush. J. Amer. Chem. Soc. **62**, 2906 (1940).
17. R. Friedel and M. Orchin. "Ultraviolet Spectra of Aromatic Compounds." New York, London, 1951.
18. W. H. Rodebush and J. Feldman. J. Amer. Chem. Soc. **68**, 896 (1946).
19. A. Kh. Khalilov and P. P. Shorygin. Zhur. Fiz. Khim. **27**, 330 (1953).
20. P. P. Shorygin and Z. S. Egorova. Doklady Akad. Nauk SSSR **117**, 856 (1957).
21. H. H. Jaffe. J. Chem. Phys. **22**, 1430 (1954).
22. H. C. Brown and V. H. Dodson. J. Amer. Chem. Soc. **79**, 2302 (1957).
23. J. R. Platt, H. B. Klevens and G. W. Schaffer. J. Chem. Phys. **15**, 598 (1947).
24. E. Jacobs, J. K. Platt and G. W. Schaeffer. J. Chem. Phys. **16**, 116 (1948).

OPTICAL INVESTIGATION OF THE MOLECULAR STRUCTURE OF CYANAMIDE AND ITS DERIVATIVES II. THE INFRARED SPECTRUM AND MOLECULAR STRUCTURE OF CYANAMIDE AND ITS SALTS

B. I. Sukhorukov and A. I. Finkel'shtein

Received 3 March 1959

The infrared (2-15μ) spectra of crystalline cyanamide and its alkaline and acid salts were obtained. The relations between frequencies were given for all investigated bondings and the calculation of the force constants and interatomic distances were carried out to a first approximation.

On the basis of experimental results the structural formulas of cyanamide and its salts have been established.

There has been recent interest in cyanamide in connection with the possibility of its utilization as a cotton plant defoliant and in the initial raw materials to obtain the polyamidic plastic. In the literature a series of works[1-3] is available in which the molecular structure of cyanamide in different compositions is studied. However, a unique solution to this question is not available.

Two structural formulas—cyanamide (I) and carbodiimide (II)—could correspond to the molecular structure of cyanamide.

$$\underset{\text{I}}{H_2N-C\equiv N} \qquad \underset{\text{II}}{H-N=C=N-H}$$

In the present work the absorption spectra are obtained in the infrared regions (2-15μ) of cyanamide crystals, deuterocyanamide, dichloride of cyanamide, cyanamide salts of calcium, zinc, lead, and silver.

The cyanamide was kindly presented by V. G. Golov and N. A. Goldberg, to whom we express deep appreciation. We obtained the dideutero-cyanide by multiple exchange with heavy water, which had been evaporated at room temperature in a desiccator over P_2O_5.

Chloride and dideuterochloride of cyanide were obtained by precipitation of cyanide chloride salts from solution with diisopropyl ether.

Cyanamide salts of zinc, lead, and silver were obtained by their precipitation from the weak solution of the alkali hydroxide. Calcium cyanamide was obtained by the reaction of calcium oxide with the dicyandiamide at 90°C and containing, according to the analysis, 87% of basic compound.

The spectra of the above substances were obtained with the help of the monochromatic spectrophotometer IKS-12 with a NaCl prism.

The samples, whose spectra were investigated had been prepared by two methods:

(1) in the form of paste with hydrocarbon (spectral region 7-15μ) and fluorinated (2-7μ) oils, and

(2) by the compression with NaCl and KBr[4] powder. In the absorption spectra of free cyanamide, obtained by the second method, strong changes were discovered. This, apparently, was due to a change in molecular structure of H_2CN_2.

This fact was not considered by Davies and Jones[3] and, as a result, the spectrum they obtained contained a series of lines related to the product of a reaction of cyanamide with the pellets of Alkali-halogen salts.

No substantial changes have been observed in the spectra of acid and basic salts, although pellets with silver cyanamide have been turning black under prolonged illumination.

Absorption spectra of crystalline cyanamide in oils is shown in Fig. 1 (T—transmission in %). In the region of NH frequency, under our experimental condition, the absorption at $\lambda_{max} = 3.07\mu$ ($\nu = 3357.3$ cm^{-1} and $\lambda_{max} = 3.15\mu$ ($\nu = 3174.6$ cm^{-1}) which we relate to $\nu_{asym(NH_2)}$ and $\nu_{sym(NH_2)}$ was detected. The decrease of these frequencies is evidently connected with the presence of hydrogen bonding and a considerable positive charge in the nitrogen atom. Davies and Jones[3] give for these frequencies the values corresponding to 3327 cm^{-1} and 3259 cm^{-1}, which seems hardly probable to us. The band at $\lambda_{max} = 3.7\mu$ is related to the combination mode and is absent in the spectrum of deuterocyanamide.

The stretching vibrations of the group ND_2 correspond to the absorption bands with $\lambda_{max} = 4.2\mu$ ($\nu = 2381$ cm^{-1} and $\lambda_{max} = 4.32\mu$ ($\nu = 2314$cm^{-1}). The first is related to $\nu_{asym(ND_2)}$ and the second to $\nu_{sym(ND_2)}$. The frequency ratio $\nu_{NH_2}/\nu_{ND_2} = 1.37$.

In the region 4.2-4.7μ a very strong absorption is observed, which is split in two components with $\lambda_{max} = 4.42\mu$ ($\nu = 2262$ cm^{-1}) and $\lambda_{max} = 4.5\mu$ ($\nu = 2222$ cm^{-1}). This splitting could be as a result of the crystalline structure of cyanamide, since it was not discovered in cyanamide solutions (we studied infrared spectra of cyanamide in nitromethane and ethyleneglycol). For deuterocyanamide it is noted that there is a small displacement of this line $\lambda_{cp} = 4.67\mu$ ($\nu = 2141$ cm^{-1}).

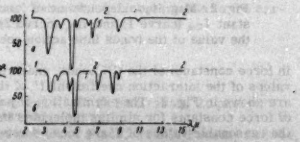


Fig. 1. Infrared spectra of crystalline cyanamide in fluorinated (1) and hydrocarbon (2) oils. a—cyanamide, b—deuterocyanamide.

In the region of 5.5-7μ two absorption bands are observed—relatively weak with $\lambda_{max} = 6.1\mu$ ($\nu = 1639$ cm^{-1}) and strong with $\lambda_{max} = 6.35\mu$ ($\nu = 1575$ cm^{-1}), corresponding to a deformation vibration of the group NH_2 ($\delta(NH_2)$), which, upon deuteriration, shifts to 8.3μ (1205 cm^{-1}).

Absorption at 6.85μ ($\nu = 1460$ cm^{-1}) appearing upon the deuteriration corresponds to the frequency of vibration of the group

Absorption at 6.1μ, in all probability, does not correspond to fundamental vibrations of the molecule H_2CN_2, since this band was absent in the spectrum of the freshly prepared deuterocyanamide. Absorption at 6.1μ was not observed either in the Raman spectrum.

We relate the symmetrical vibration of the skeleton to the absorption band at λ_{max} = 8.77μ (ν = 1140 cm^{-1}) which, upon deuteriration, shifts very insignificantly. The appearance of a band with λ_{max} = 10.8μ (926 cm^{-1}) we relate to ν_{rock} deformation vibration of the group NH_2. The frequencies of the remaining vibrational degrees of freedom of cyanamide are as follows: ν_{wag}, rocking or wagging vibration of the group NH_2; in-plane and out-of-plane vibration of the group N—C ≡ N are located beyond 15μ. To these vibrations, as follows from references 1 and 2, correspond the frequencies ν_ω (638 cm^{-1}), γ_{NCN} (522 cm^{-1}), and δ_{NCN} = (429 cm^{-1}).

From the above spectrum interpretation, it is seen that the structure I corresponds to the molecular structure of the crystalline cyanamide.

From the data of the vibrational frequencies it appears possible to calculate the set of structural parameters of the molecule. However, the absence of data of interatomic distances and angles does not make it possible to calculate theoretically the complete spectrum of H_2CN_2 and to determine all the force constants of the molecule. Nevertheless, it is possible, at first approximation, to represent the molecule of the cyanamide as a three-mass model (m_1—NH_2; m_2—C; m_3—N).

The calculation of the quasi-elastic constants with the help of known frequency equations gives for the force constants of the CN bonds the values 16×10^5 dynes/cm for one and 7.5×10^5 dynes/cm for the other bond (under the assumption that the force interaction coefficient of these bonds is equal to 1.0×10^5 dynes/cm. The changes

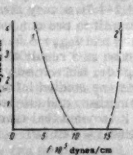


Fig. 2. Magnitude dependence of force constant f_{CN_1} (curve 1) and f_{CN_2} (curve 2) from the value of the bonds interaction coefficient f'.

in force constants of the CN bonds, under the different values of the interaction coefficient f' of these bonds, are shown in Fig. 2. The examination of published data of force constants for similar molecules indicates that the reasonable values of f' are located between 0.4 and 1.5×10^5 dynes/cm, whereupon the most probable value should be close to 1×10^5 dynes/cm.

It should be indicated that the quasielastic constants, as calculated by Davies and Jones,[2] have hardly plausible values. For example, considering that the quasi-elastic constant of the CN triple bond equals 17.0×10^5 dynes/cm, those authors obtained, for the other CN bond, a value for the quasi-elastic constant of 18.3, and, for the constant of the bond's interaction, the value of 5.1×10^5 dynes/cm.

If the other admissible values of the quasi-elastic constant of a triple bond are used, then the same absurd values would be obtained for the force interaction constant and quasi-elastic constant of the CN double bond. The value of the quasi-elastic constants of the CN bonds, as deduced by the foregoing authors, forces the conclusion that the investigated molecules have carbodiimide structure II. Yet the authors do not come to this conclusion, but explain such high and close values of the CN quasi-elastic constants as the effect of hyperconjugation. This explanation does not appear compatible, as the hyperconjugation cannot increase the force constant by the factor of 3.

The values of force constants, as obtained in reference 2, can be explained by referring wrongly to the line at λ_{max} = 6.35μ (ν = 1575 cm^{-1}) to S-vibration of molecular skeleton. As was indicated above, we associate with the symmetrical vibration of the skeleton the band at λ_{max} = 8.71μ (ν = 1140 cm^{-1}). Such an interpretation of frequencies gives the acceptable magnitude of the force constants, which confirm the nonequal value of the C—N bonds.

For the calculation of interatomic distances, Badger's equation[7]

$$f(r_i - d_{ij})^3 = c_{ij}, \qquad (1)$$

has been utilized where d_{ij} and c_{ij} are constants, equal to 0.667 and 2.07 respectively, which we have determined from the data[10] for different molecules containing single, double, and triple bonds.

From the above derived values of f r_{CN_1} = 1.32 ± 0.03 A and r_{CN_2} = 1.172 ± 0.006 A are obtained. The numbers ±0.03 and ±0.006 were obtained by variation of f' in the limits 0.4-4.5 × 10^5 dynes/cm.

For the accepted model the deformational coefficient of elasticity turned out to be equal to 0.3 × 10^5 dynes/cm.

From the obtained force constants, the orders of the bonds n have been determined according to the formula

$$n = a + bf. \qquad (2)$$

The constants a and b can be determined from the data for methylamine (n = 1, f = 4.77 × 10^5 dynes/cm) and HCN (n = 3; f = 18.6 × 10^5 dynes/cm). The calculation gives n_{CN_1} = 1.40; n_{CN_2} = 2.62. The sum of the bond orders for the carbon atom is equal to 4.02.

Utilizing the system of supplementary conditional designation,[8] the structural formula of cyanamide in crystalline state can be represented in the following form:

$$H_2\overset{(+)}{N} \rightarrow C \cong \overset{(-)}{N}.$$

The question regarding the molecular structure of cyanamide salts will now be investigated. Figure 3 shows the spectra of cyanamide salts compressed with KBr. The spectrum of a calcium cyanamide shows an intensive absorption band at λ_{max} = 4.95μ (2022 cm^{-1}) which we relate to the antisymmetric vibration of the ion $(NCN)^{--}$. By comparison with a corresponding vibration of a free cyanamide this band is displaced toward a long wavelength region. Two others absorption bands at 7.5μ (1259 cm^{-1}) and 10.75μ (930 cm^{-1}) have a weak intensity. It seems that one of these frequencies refers to ν_s. If it is assumed that ν_s = 930 cm^{-1} then the inacceptable values (imaginary, negative, or too high) are obtained for the force constants, both for symmetrical and nonsymmetrical models. But calculating with ν_s = 1259 cm^{-1}, then the acceptable value of the interaction coefficient f' of the bonds is f' = 1.42 × 10^5 dynes/cm, which can be obtained only for the symmetrical model. Then, f_{CN_1} = f_{CN_2} = 10.2 × 10^5 dynes/cm which is closer to the value f for the double bond C=N, as calculated by Japanese authors.

The calculation by Badger's formula (1), using the constants d_{ij} = 0.667 and c_{ij} = 2.07 computed from data given in reference 10, gives for the distance C—N r_{CN} = 1.255 A. The x-ray investigations[5] also lead toward the symmetrical model with the interatomic distance r_{CN} = 1.25 ± 0.01 A which is close to the value which we found.

The frequency 930 cm^{-1} can be interpreted as the overtone of the deformation vibration. In this case the deformation force coefficient $f_\alpha / r^2_{CN} = 0.27 \times 10^5$ dynes/cm.

The absorption spectra of the other salts (cyanamide, zinc, and lead) are very close to the calcium cyanamide, which indicates the proximity of the field of force. In the silver cyanamide splitting is observed in two bands, which can be explained by Fermi's resonance with $2\nu_{def}$.

It is interesting to note the following regularity: with the increase of the intensity in the observed line ν_5, the intensity of the line ν_{a_1} decreases. In particular, the frequency ν_5 is not observed in zinc cyanamide, but the intensity band ν_{a_1} is the largest. The appearance of the forbidden band ν_ζ could be correlated with some changes in the molecular symmetry due to the field interaction of the neighboring crystal's molecule. From the foregoing, it follows that the structure of the cyanamide anion can be represented by the structural formula

$$\bar{N}=C=\bar{N}.$$

Figure 4 shows the spectra of a dichloride cyanamide and a dideuterodichloride cyanamide compressed with sodium chloride. The spectra of these salts, obtained in a form of a paste in oils, coincide with the spectra of Fig. 4. The spectra comparison of the indicated salts permits the frequencies to be related with the following vibration:

$$\nu_{as(NH_2)} = 3205 \text{ cm}^{-1}, \ \nu_{s(NH_2)} = 2985 \text{ cm}^{-1} \text{ and } \nu_{\delta(NH_2)} = 1420 \text{ cm}^{-1}.$$

In the spectrum of dideuterodichloro cyanamide a series of frequencies corresponding to ND_2-, as well as to the NHD vibration is observed.

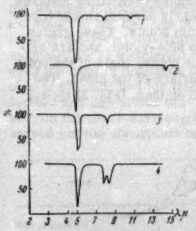


Fig. 3

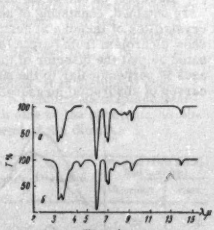


Fig. 4

Fig. 3. Infrared spectra of cyanamide salts compressed with KBr. 1—calcium cyanamide, 2—zinc cyanamide, 3—lead cyanamide, 4—silver cyanamide.

Fig. 4. Infrared spectra of cyanamide derivatives, compressed with NaCl. a—cyanamide of dichloride, b—cyanamide of dideuterodichloride.

The frequencies $\nu_{as(NCN)} = 1680$ cm^{-1} and $\nu_{s(NCN)} = 1075$ cm^{-1} are related to the skeleton vibration. Calculations according to a three-mass model, gives: $f_{CN} = f_{CN_\zeta} = 7.26 \times 10^5$ dynes/cm, $f' = 1.77 \times 10^5$ dynes/cm. The calculation of the interatomic distances by Badger's formula (1), using the constants d_{ij} and c_{ij}, the same as for calcium cyanamide gives $r_e = 1.32$ A.

An intensive band in the region 2500-2700 cm^{-1} was not detected to any degree, which could be attributed to H—Cl vibration. From this it follows that by salt formation, protons totally (or almost totally) move over to the nitrogen. This is confirmed by the presence of two bands —3205 and 2985 cm^{-1}—which could be attributed only to antisymmetric and symmetric vibrations of the NH_2 group. Thus, the structural formula of the dichloro cyanamide should have the form

$$|H_2\bar{N}=C=\bar{N}H_2|Cl_2^{--}.$$

Having obtained the data for the force constants of the cyanamide's anion and cation, it is possible to calculate the spectrum of cyanamide in carbodiimide form HN = CNH, by taking into account that the values of the force constants in this molecule have the intermediate values characteristic to the ions $\bar{N}C\bar{N}$ and $H_2\bar{N}CNH_2$ ($f_{C\bar{N}} = 8.72 \times 10^5$ dynes/cm and $f' = 1.60 \times 10^5$ dynes/cm). In this case the values are obtained for the skeleton vibrations in carbodiimide form $\nu_{a_1} = 1858$ cm^{-1}, $\nu_\zeta = 1165$ cm^{-1} and for interatomic distance 1.288 A.

It seems that the observed value of the frequency ν_{a_1} in carbodiimide form apparently is lowered, as the value $\nu_{as(NCN)}$ in the alkyl substituted R—N=C=N—R is located between 3125 and 2140 cm^{-1}.[11]

The regularity of variation of the interatomic distance in the series $\bar{N}CN$, HN=C=NH, and $H_2\bar{N}CNH_2$ can easily be explained as the variation in the degree of ionic bonds C=N in this series. Data obtained for the force constants and interatomic distances are to the first approximation and in the future will be defined more accurately.

CONCLUSION

1. The infrared spectra of the crystalline cyanamide and its alkaline and acid salts have been obtained.

2. The relations between frequencies are given and the force constants and interatomic distances in indicated compounds are calculated, to the first approximation. The structural formulas of the cyanamide (with the determination of the order of the bonds) and its salts were derived.

3. On the basis of the investigation spectra of the cyanamide salts are given along with the evaluation of the significance of the skeleton frequencies, force constants, and interatomic distances of the cyanamide in the carbodiimide form.

REFERENCES

1. L. Kahovec and K. W. F. Kohlraush. Z. physik. Chem. 1337, 421 (1937).
2. M. Davies and W. J. Jones. Trans. Faraday Soc. 54, 1454 (1958).
3. A. Franssen. Bull. Soc. chim. France 4, 63 (1928).
4. R. D. Barnard. Ohio J. Sci. 48, 189 (1948).
5. J. Jamamoto, Kz. Kinoshita, K. Tamura, and T. Jamanaka. Bull. Chem. Soc. Japan. 31, 501 (1958).
6. A. I. Finkelstein, F. L. Malachevskaya, A. M. Fisher, and B. G. Rabovski. Opt. i Spektr. 6, 415 (1959); Opt. i Spektr. 6, 415 (1959).
7. R. W. Badger. J. Chem. Phys. 3, 128 (1934).
8. A. I. Finkelstein. J. Phys. Chem. 31, 1659, (1957); Zhur. Fiz. Khim. 31, 1659 (1957).
9. H. Siebert. Z. anorg. Chem. 273, 170 (1953).
10. W. J. Orville-Thomas. Chem. Rev. 57, 1179 (1957).
11. G. D. Meokins and R. J. Moss. J. Chem. Soc. 993 (1957).

ON SOME PECULIARITIES OF THE ABSORPTION SPECTRA OF CRYSTALS AND SOLUTIONS OF THIONINE VIOLET

N. M. Melankholin and E. N. Slavnova

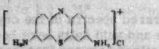
Received 23 April 1959

Absorption spectra of crystals of thionine were investigated. Two different modifications were identified by spectrophotometric means, both crystallizing from water solutions. From the solution containing lead nitrate, crystals of a dye were obtained which were different from the modifications mentioned.

The dependence of the absorption curves of the water solutions of thiazine dyes on the presence of nondisplaced atoms of hydrogen in the amino groups of its complex ions, was discovered. In solutions containing lead nitrate, a change in the shape of the absorption curve was observed, on increase in concentration of the dye. In such solutions of thionine, and in certain other relations, something is involved other than a different thiazine dye.

The observed peculiarities of the absorption spectra and other properties of thionine, distinguishing it from other thiazine dyes, can be explained by the possibility of nondisplaced atoms of hydrogen in the amino groups forming hydrogen bonds in a crystalline dye, just as in water solutions.

Of all the thiazine dyes, thionine (Lauth's violet) has an especially simple structure



In other dyes of this group, the atoms of hydrogen in the amino groups are partially or entirely replaced by methyl and ethyl groups, which makes the molecule more complicated. Investigating the absorption spectra of crystals of the dyes mentioned, we expected that the simplicity of structure of the molecule of thionine would consequently also affect the simplicity of the absorption spectra of its crystals. Such a dependence we have already established in methylene blue,[1] which also has a relatively simple and symmetrical structure.*

*In crystals of methylene blue, each of the absorption curves due to oscillations parallel to the main optical axis has, within the limits of the visible spectrum, only one maximum. For crystals of other thiazine dyes, analogous curves ordinarily have several maxima; that is, they are more complex.

Absorption curves were measured by us for different thionine crystals by use of a photoelectric microspectrophotometer.[2] In the investigation, samples in which thionine crystals were formed by slow evaporation of a drop of the water solution of the dye, applied to a glass plate, were used. In such preparations, the crystals that are formed are always needle-shaped, often parallel, or radial in disposal about the points of contact. Those that are joined parallel, showing dichroism, range from brownish yellow to dark purple, and are usually oriented so that the plane of the axes N_gN_p lies parallel to the glass. Figure 1 shows the absorption curves for vibrations parallel to the axes N_g and N_p, measured along such a direction. Absorption curves for oscillations parallel to N_g have 4 maxima at about 460, 540, 602, and 700 mμ; an especially intense absorption band lies at 602 mμ. Another absorption curve for the same crystals has one wide band of absorption at 492 mμ, in which there is a barely noticeable second maximum at about 460 mμ. Thus the absorption spectra of crystals of thionine are found to be fairly complex, and in any case, more complex than for crystals of methylene blue. This forces one to conclude that crystals of thionine have a different structure; and possibly they also have a different intermolecular bond.

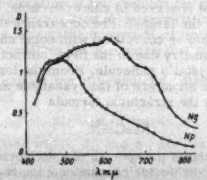


Fig. 1. Curves of absorption parallel to the junction of thionine crystals.

However, on one of the samples crystalline textures were obtained, consisting of nearly parallel thread-like crystallites of thionine at certain points. These grains show dichroism from purple to blue-violet, and are oriented so that the bisector of the obtuse angle of the optic axes is perpendicular to the surface of the glass. The curves of absorption measured on them (Fig. 2) appear

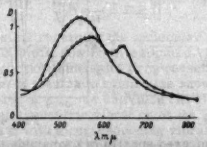


Fig. 2. Curves of absorption of a thionine grain.

simpler than the curves of Fig. 1; on one of them only one absorption band is visible, with a maximum at 548 mμ; on the other, there are two bands with maxima at 572 and 645 mμ.

In Figs. 1 and 2 we see four absorption curves of oscillations parallel to the principle axes; it follows from the last analysis that two of these should be similar to the other two but, in fact, no curve in Fig. 2 is similar to any curve in Fig. 1. From this it may be concluded that here there are evidently two different crystal modifications. In other investigations of thiazine and oxazine dyes by us, we observed no different modifications; therefore, in this respect, thionine is different from the other thiazine dyes.

In addition to the two forms of crystals described above, absorption spectra were investigated for relatively

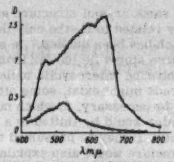
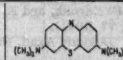
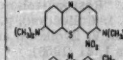
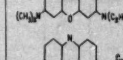
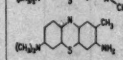
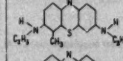
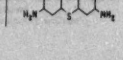


Fig. 3. Curves of the absorption of crystals of thionine grown from a solution containing lead nitrate.

large crystals grown from a solution containing lead nitrate. These absorption curves (Fig. 3) are different from those presented above (Figs. 1 and 2) although the upper curve in Fig. 3 in its short wavelength part is close to the upper curve of Fig. 1. It would seem that these crystals correspond to some other state of the dye, occurring only in the presence of lead nitrate, as the result of an interaction with it. In other thiazine dyes, crystals obtained from solutions with lead nitrate are not different in their optical properties from crystals obtained from the pure solutions.

The difference of thionine from other thiazine and oxazine dyes is observed not only in the absorption spectra of the crystals, but in the absorption spectra of the water solutions.

Absorption spectra of the water solutions of thiazine dyes have been often published by different investigators,[3] and have often been obtained by us using a self-recording spectrophotometer SF-2-M. Each of these spectra has two absorption bands corresponding to the presence in the solution of complex ions (cations) of the monomer and the dimer of the dye. As is evident from the Table, in most of the dyes investigated, the absorption bands of the monomer lie at wavelengths 656-668 mμ; in two of the dyes the band is displaced toward the short wavelength side to 636 mμ; and for thionine, it is displaced even further and lies at 602 mμ. An analogous displacement, also on the short wavelength side of the spectrum, is observed for the absorption band of the dimer.

Dye	Formula of the cation	Position of the absorption band (mμ)	
		monomer	dimer
Methylene blue		656	600
Methylene green		658	606
Capri blue		658	606
Thionine blue		668	610
Toluidine blue		636	582
Novomethylene blue		636	596
Thionine blue		602	563

Thus the absorption spectra of thionine solutions, maintaining the general pattern of the absorption spectra of thiazine dyes, are substantially different from those in the position of the absorption bands.

Solutions of thionine (as well as those of other thiazine dyes) were also used for investigation of the process of entrapment of the dye, by growing grains of crystals of lead nitrate and barium nitrate.[4,5] In this connection absorption curves were obtained for saturated solutions of the nitrates with additions of dye in different concentrations. As a result of such investigations, the following pecularities were observed for thionine.

In contrast with other thiazine dyes, thionine is not absorbed by growing crystals of the nitrates.

In adding to the solution of thionine (with concentrations of the order of 0.01% and more) increments of lead nitrate up to saturation of the solution by the nitrate, the dye partly separates out in the form of crystals, which is not observed in the case of other thiazine dyes for such small concentrations. This indicates the low solubility of thionine crystals.

For concentrations of thionine of 0.2% and above, the form of the absorption curve of the solution changes sharply. In place of the curves such as observed for the lower concentrations—an absorption band of the dimer at 562 mμ—a new band appears which is displaced from 550 to 540 mμ with increasing concentrations of the dye (Fig. 4). This band is markedly broadened in comparison with the dimer absorption band. The new band appears both in solutions with lead nitrate, and also in solutions with barium nitrate.

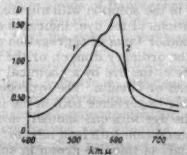


Fig. 4. Absorption curves of thionine solutions containing lead nitrate, for different concentrations of the dye. Concentrations: curve 1—0.2%, curve 2—0.02%.

The sources of the peculiarities in the absorption spectrum of thionine, noted above, must be sought in the structure and properties of its molecules, or more precisely, in its complex cation, which is also a center of light absorption. The cation of thionine has, on both sides, amino groups containing atoms of hydrogen. This, on the one hand, renders it the simplest of the cations of all the thiazine dyes, and on the other, imparts to it special properties. Atoms of hydrogen bonded with nitrogen are more active than those bonded with carbon since the former element readily forms hydrogen bonds. In the dye solution it forms an ordinary carbon bond N—H—O with molecules of water, making a complex with the dye cation. Consequently the bonds within such a complex with thionine are more stable than with other thianine dyes in which the bonds are only van der Waals bonds. The stiffening of these bonds leads also to a displacement of the energy levels of the cation of thionine, that is, to a displacement of the absorption bands of the solution. In support of such an explanation, the fact may be pointed out that in toluidine blue and novomethylene blue, in which the active atoms of hydrogen are only partially replaced by methylene and ethylene groups (see the Table),

the absorption bands are also displaced in the short wavelength direction, but only to 636 mμ, that is, less than with thionine.

The fact that for a series of dyes (the first four dyes in the table above) the position of the absorption band of the monomer is nearly the same, indicates that this band is hardly dependent on the composition of the replacing group, if all of the active hydrogen atoms are displaced. It also does not depend on the presence, or absence of additional groups in the ortho position to the amino group (methylene green), nor on the replacement of sulfur by oxygen in the skeleton of the cation itself (Capri blue). This confirms the fact that the absorption of light by the cations of thiazine dyes in the visible spectrum depends basically, for all these dyes, on the conjugate bonds of the chain which extends along the cation through the nitrogen atom in the heterocyclic compound. The shifting of the absorption band when the hydrogen bond is present is explained by the fact that the formation of a more stable bond with molecules of water produces tighter bonds in the coupled system itself.

The shift of hydrogen itself in methylene and ethylene groups, which, as is well-known, causes the batho-chrome effect in other cases. However, in Capri blue, a similar shift takes place at the very end of the conjugated chain which controls the absorption of light by the ion, and still the absorption band of this dye is hardly shifted at all in relation to that of methylene blue. Therefore in this case, we consider it more acceptable to explain the shift in the absorption band by the influence of the hydrogen bonds.

The shift of the absorption band of the dimer (from 562 to 540 mμ) in the solution with nitrate, for sufficiently large concentrations of the dye, indicates either the development of another form of aggregation of the molecule (in addition to the ordinary dimer), or the formation of some other state of the dye by a chemical interaction with the nitrate of lead or barium. The hydrogen bond might have considerable importance both in the interaction of the cations of the dye with one another, and also in the case of their interaction with lead nitrate. It was shown above that crystals of thionine grown in solutions with lead nitrate have an absorption spectrum different from that of crystals grown in a pure dye solution. It is possible that these crystals grow precisely by reason of this new state of the dye.

As for the nature of the pecularities of the absorption spectra of pure crystals of thionine, one should notice that the possibility of forming hydrogen bonds may exist in the crystal lattice. Active atoms of hydrogen may form hydrogen bonds with atoms of nitrogen in neighboring heterocyclic cations, and possibly also with molecules of water of crystallization, the presence of which is characteristic of crystals of thiazine dyes. However, the existence of a hydrogen bond between molecules of the dye in a crystal is not possible if one assumes that thionine has the same crystal structure as that of methylene blue, closely related to it—the only thiazine dye the structure of which has been studied.[5] In such a structure, the active hydrogen atoms lie too far from the atoms of nitrogen in neighboring heterocyclic molecules. In order that hydrogen bonds might exist, some other crystal structure would be necessary, in which neighboring series of molecules would be shifted to a half period relative to each other. It may be presumed that precisely such another structure would also explain the relative complexity of the absorption spectra of thionine crystals, in view of the simplicity of its molecules. The lower solubility of crystals of thionine in comparison with other thiazine dyes can also be explained by the presence of intermolecular hydrogen bonds in its crystal lattice.

The second crystalline modification of thionine, having a simpler absorption spectrum, apparently has a structure similar to the structure of methylene blue, for which hydrogen bonds between neighboring molecules is not possible. Proof of this surmise must be established by study of the structure of thionine crystals, which has not yet been done. The fact that thionine, in contrast with other thiazine dyes, is not absorbed by growing crystals of lead nitrate can also be explained as the result of the presence of active atoms of hydrogen. It may be presumed that absorption of molecules of the dye is prevented by the strong hydrogen bonds between the dye molecules and molecules of water. Absorption to the growing grain of the whole dye-water complex cannot occur because the nitrate crystals do not contain water of crystallization. Such a presumption is supported by the fact that novomethylene blue, the molecule of which has only two active atoms of hydrogen, is less adsorbed by crystals of nitrates than other thiazine dyes.

Thus the pecularities of the absorption spectra that have been observed by us, and also certain other properties of thionine, differentiating it from the other thiazine dyes, can be explained by properties of the complex cation, in its ability to form hydrogen bonds both in its water solutions, and in its crystals.

REFERENCES

1. N. M. Melankholin. Opt. i spektr. 3, 104 (1957).
2. N. M. Melankholin and B. N. Grechushnikov. Trudy Inst. Kristollogr. No. 12, 186 (1956).
3. L. F. Epstein, F. Karush, and E. Rabinowitch. J. Opt. Soc. Am. 31, 1, 77 (1941).
4. E. N. Slavnova. Doklady Akad. Nauk SSSR 106, 1007 (1956).
5. E. N. Slavnova. "Rost kristollov I, Sbornik." (Growing of Crystals. I. Collection), p. 149, 1957.
6. G. S. Zhdanov, Z. V. Zvolkova, and L. G. Vorontsova. Kristallografiya 1, 61 (1956).

QUANTUM YIELDS OF PHOSPHORESCENCE AND FLUORESCENCE OF SOME 1-DERIVATIVES OF NAPHTHALENE IN SOLUTIONS AT −196°C

V. L. Ermolaev and K. K. Svitashev

Received 11 March 1959

An investigation of inner conversion processes in organic molecules from an excited singlet to a triplet state presents considerable interest. Competition of this process with fluorescence and nonradiative quenching determines the fraction of excited molecules appearing in the triplet state, which is supposed to take part in many important photochemical reactions,[1] including photosynthesis.[2] One of the methods of investigation of inner conversion processes consists of the study of the ratio of quantum yields of phosphorescence and fluorescence of organic molecules in solid solutions at liquid nitrogen temperature. We undertook in the present work the investigation of the influence of some substitutes in the 1 position of a naphthalene structure on the relative probability of conversion to the matastable state.

The measurements were made on a photoelectric apparatus consisting of a monochromator with a diffraction grating (relative aperture 1:4, second-order dispersion 15 A per mm), a photomultiplier FEU-18, and an electronic recording potentiometer EPPV-51. The apparatus was calibrated for spectral quantum sensitivity by means of a Tungsten incandescent lamp. The excitation of luminescence was achieved, using the radiation of mercury lines, 3030 or 3130 A, also with the help of a diffraction grating monochromator.

In order to determine the ratio of the quantum yields of fluorescence and phosphorescence (η_{ph}/η_{fl}), a quotient was calculated of the area of the phosphorescence spectrum, expressed in quantum intensity, by the area of the fluorescence spectrum brought to the same scale. The large distance separating the phosphorescence spectrum of the investigated naphthalene derivatives (22000–17000 cm^{-1}) from their fluorescence spectrum (32000–27000 cm^{-1}) permitted the spectra to be separated by means of light filters (ZhS-11 and UFS-2) during stationary illumination, without recourse to a phosphoroscope. A correction was applied for the change of the refractive index of the solvent when a shifting was made from the spectral region of phosphorescence to the region of fluorescence emission. The comparison of the quantum yields of luminescence of various substances was done in the same apparatus by the method of equal absorption. A mixture of ethanol ether (2:1 by volume; Alc – Et) or petroleum ether (P. E.) were used as solvents, which froze to a glassy consistency at the temperature of the experiment (−196°C). The substances and the solvents were carefully purified by distillation in air and in vacuum.*

*The purification of solvents was described in more detail in a previous article by one of the authors.[3]

The papers by McClure, Gilmore, and Gibson,[4] Sveshnikov,[5] Neporent and Inyushin,[6] and Zelinskii and Kolobkov[7] deal with the measurement of relative phosphorescence yields. In reference 4 measurements of absolute quantum yields of some substances at liquid nitrogen temperature are also reported. We determined the absolute quantum yields of fluorescence and phosphorescence from the relative yields by using the data of Gilmore et al.[4] for the absolute quantum yield of naphthalene fluorescence.

The following derivatives of naphthalene were investigated: naphthalene, 1-fluoro-naphthalene, 1-chloro-naphthalene, 1-bromo-naphthalene, 1-iodo-naphthalene, 1-methyl-naphthalene, 1-oxy-naphthalene, 1-naphthaldehyde, 1-nitro-naphthalene, and quinoline, a heterocyclic analog of naphthalene. The results of our measurements are shown in the table.

Quantum Yields of Phosphorescence and Fluorescence of 1-Derivatives of Npahthalene at −196°C

Compound	ν_{fl}^{max} (cm^{-1}) Alc + Et	ν_{ph}^{max} (cm^{-1}) Alc + Et	η_{fl} Absolute Alc + Et	η_{ph} Absolute Alc + Et	η_{ph}/η_{fl} Alc + Et	η_{ph}/η_{fl} P.E.	τ_{ph}(sec) Alc + Et	$1/\tau_0$ (sec^{-1}) $S^0 \to S$	$1/\tau_1$ (sec^{-1}) $S \to T$
Naphthalene	31750	21250	0.55 **	0.051 ± 0.003	0.093 ± 0.006	0.084 ± 0.004	2.3 ± 0.1	$\sim 10^{8}$***	$\sim 10^{8}$
1-fluoro-naphthalene	31600	21150	0.84 ± 0.08	0.056 ± 0.010	0.068 ± 0.004	—	1.5***	$\sim 3 \cdot 10^{8}$***	$\sim 2 \cdot 10^{8}$
1-chloro-naphthalene	31360	20700	0.058 ± 0.005	0.30 ± 0.06	5.2 ± 0.5	—	0.29 ± 0.01	$\sim 3 \cdot 10^{8}$***	$\sim 1.5 \cdot 10^{9}$
1-bromo-naphthalene	31280	20650	0.0016 ± 0.0005	0.27 ± 0.04	164 ± 21	193 ± 25	$2 \cdot 10^{-4}$***	$\sim 3 \cdot 10^{8}$***	$\sim 5 \cdot 10^{8}$
1-iodo-naphthalene	—	20500	< 0.0005	0.38 ± 0.06	> 1000	—	$(2.0 \pm 0.2) \cdot 10^{-9}$	$\sim 3 \cdot 10^{8}$***	$> 3 \cdot 10^{8}$
1-methyl-naphthalene	31450	21000	0.85 ± 0.19	0.044 ± 0.013	0.053 ± 0.002	—	2.1 ± 0.1	$\sim 3 \cdot 10^{8}$	$\sim 2 \cdot 10^{8}$
1-oxy-naphthalene	30775	20800	0.76 ± 0.04	0.036 ± 0.004	0.047 ± 0.002	0.056 ± 0.004	1.9***	$\sim 3 \cdot 10^{8}$	$\sim 2 \cdot 10^{8}$
1-naphthaldehyde	—	19750	< 0.0001	0.02 ± 0.01	> 200	—	$(8 \pm 1) \cdot 10^{-9}$	—	—
1-nitro-naphthalene	—	19250	< 0.0001	0.083 ± 0.017	> 1000	—	$4.9 \cdot 10^{-9}$***	—	—
Quinoline	31925	21800	0.100 ± 0.005	0.19 ± 0.02	1.9 ± 0.1	> 100	1.4 ± 0.1	—	—

*The light of the levels determined from the location of the shortwave band maximum of the fluorescence or phosphorescence spectrum. The accuracy is ±25 cm^{-1}.

**Absolute quantum yield of naphthalene fluorescence according to data by Gilmore, Gibson and McClure, from which the remaining absolute quantum yields were determined.

***According to data by McClure[4].

In the first place, we were interested to know how the probability of inner conversion to the metastable state changes when a heavy atom is introduced into the molecule. It was shown in the paper by Sponer and Teller that the probabilities of forbidden intercombination transitions in molecules are basically determined by the heaviest atom entering the molecule. McClure,[3] while investigating phosphorescence decay-times of a series of halogen substituted aromatic compounds, has experimentally demonstrated the fast increase of the probability of triplet-singlet radiation in the sequence of fluoro-, chloro-, bromo-, and iodo-derivatives of nahpthalene and benzene. It is interesting to trace how the introduction of a heavy atom influences the probability of a nonradiative intercombination transition from an excited singlet state to the lowest triplet state of the molecule. It was shown by Gilmore et al.,[4] with the halogen derivatives of benzene, that the introduction of a heavy atom not only decreases the decay time of phosphorescence, but also increases the ratio of the quantum yields of phosphorescence and fluorescence. However the data of their paper do not permit a qualitative comparison of the probability of phosphorescence radiation and the probability of inner conversion upon introduction of a heavy atom.

The series of halogen derivatives of naphthalene is the most convenient subject for such a comparison. The table shows our data on absolute quantum yields and on the ratio of the yields of phosphorescence and of fluorescence of this series, as well as other properties of the investigated molecules, such as the heights of the fluorescent and phosphorescent levels, the decay time, and the probability of the radiative transition $S^* - S$. One can see in the fifth column of the table that the relative yield of phorphorescence increases rapidly in the sequence of fluoro-, chloro-, bromo-, and iodo-naphthalenes. A certain decrease of the relative yield of phosphorescence takes place when naphthalene is replaced by 1-fluoro-naphthalene and also by 1-oxy- and 1-methyl-naphthalene. This decrease is apparently connected not with the decrease of the value of the probability of inner conversion, but with the increase of the probability of the radiative transition $S^* - S$. The radiative transition between the ground and the first excited singlet level is forbidden in naphthalene because of symmetry considerations (the oscillator strength of the transition $f \sim 0.001$, $\tau_a \cong 10^{-6}$ sec); this prohibition is partially lifted in 1- derivatives of naphthalene, and the oscillator strength of the first absorption band increases 3 to 4 times ($f \sim 0.003$, $\tau_a \cong 3.0 \times 10^{-7}$ sec).

Knowing the probability of a radiative transition in naphthalene and its derivatives, and assuming no quenching on the triplet level in solid solution, one can estimate the probability of inner conversion to the triplet level, and the change in probability upon introduction of a heavy atom. Data of such a rough estimate are shown in the last column of the table. The comparison of these data with the probability of a radiative $(T - S)$ transition, estimated from the decay time of phorphorescence (τ_{ph}, in the table), shows that the increase in inner conversion probability with the introduction of a heavy atom takes place faster than the increase in the probability of a radiative transition $T - S$. Shifting from fluorine to chlorine, from chlorine to bromine etc., the probability of phosphorescence emission increases approximately 10 times at each step, while the probability of inner conversion increases approximately 35 to 70 times.

In so far as it was shown in the articles of Zelinskii and Kolobkov[5] that the value of the relative yield of phosphorescence of phthalimide derivatives and some other substances depends on the solvent used, we conducted the measurements of the ratio of the yields of phosphorescence and fluorescence not only in the Alc – Et. mixture (a polar solvent), but also in P. E. (a nonpolar solvent), solidifying to a glassy state. The data η_{ph}/η_{fl} in P.E. are entered in the sixth column of the table. Their comparison with the data for the Alc. – Et. mixture shows that the change in the relative yields of phosphorescence is small in all investigated cases, with exception of quinoline. Quinoline has in an Alc. – Et. mixture a noticeably larger yield of phorphorescence than naphthalene (approximately 20 times more). Therefore, besides the introduction into the molecules of a heavy atom, a large increase in the probability of inner conversion is also brought about by the inclusion in the naphthalene ring of a nitrogen molecule having free electrons. In P. E. quinoline only phosphoreses, the florescence being totally absent; i.e., in the case of quinoline the solvent can very noticeably influence the probability of inner conversion to a metastable state. We assume that this influence is due to the presence or absence of hydrogen bonds between the nitrogen atom of the quinoline molecule and the OH group of the solvent. The presence of hydrogen bonds between nitrogen and hydrogen apparently decreases the influence of free n-electrons of the nitrogen on the π-cloud of the quinoline molecule, and thus decreases the spin-orbital interaction in the molecule, favoring emission of phosphorescent radiation.

The large probability of inner conversion on the triplet level in 1-naphthaldehyde and 1-nitro-naphthalene is also tied to the influence of free electrons of the $-C=O$ and $-NO_2$ groups. However, it is already quite difficult to find an analogy between these molecules and the molecule of naphthalene, insofar as the absorption spectrum in them is strongly modified compared to the simplest naphthalene derivatives. Moreover, in these molecules a coupling between the double bonds appears in the substitutes and the π-cloud of the ring, and the n-π transitions in the substituting groups also show up. A substantial part must be played in the case of 1-naphthaldehyde by the intramolecular energy transfer along the triplet level, as it is assumed in the article of Terenin and of one of the authors.[10]

In conclusion, we consider it a pleasant privilege to express our deep gratitude to the Academician A. N. Terenin, under whose direct guidance this work was done. We also express our gratitude to A. T. Troshchenko, who kindly supplied us with 1-fluoro-naphthalene.

REFERENCES

1. A. N. Terenin. "Fotokhimiya krasitelei i rodstvennykh organicheskikh soedinenii." (Photochemistry of Dyes and Related Organic Compounds), Izd. Akad. Nauk SSSR, 1947;
G. Oster and A. H. Adelman. J. Am. Chem. Soc. 78, 913, 3977 (1956).
2. A. N. Terenin. "Fotokhimiya khlorofilla i fotosintez, VI Bakhovskie chteniya." (Photochemistry of Chlorophyll and the Photosynthesis, 6th Bach Lecture). Izd. Akad. Nauk SSSR, 1955;
J. Franck. Proc. Natl. Acad. Sci. U.S. 44, 941 (1958).
3. V. L. Ermolaev. Opt. i Spektr. 1, 523 (1956).
4. E. H. Gilmore, G. E. Gibson, and D. S. McClure. J. Chem. Phys. 20, 829 (1952); J. Chem. Phys. 23, 399 (1955).
5. B. Ya. Sveshnikov. "Fosforestsentsiya organicheskikh soedinenii." (Phosphorescence of Organic Compounds), Dokt. diss., Fiz. Inst. Akad. Nauk USSR, 1951.

6. B. S. Neporent and A. I. Inyushin. Doklady Akad. Nauk SSSR 98, 197 (1954).
7. V. V. Zelinskii and V. P. Kolobkov. Doklady Akad. Nauk SSSR 101, 241 (1955); Doklady Akad. Nauk SSSR 119, 922 (1958);
V. V. Zelinskii, V. P. Kolobkov, and I. I. Reznikova. Doklady Akad. Nauk SSSR 121, 315 (1958);
L. E. Golikova, V. V. Zelinskii, and V. P. Kolobkov. Opt. I. Spektr. 5, 480 (1958).
8. H. Sponer and E. Teller. Revs. Modern Phys. 13, 75 (1941).
9. D. S. McClure. J. Chem. Phys. 17, 905 (1949).
10. V. L. Ermolaev and A. I. Terenin. J. chim. phys. et phys.-chim. biol. 55, 698 (1958).

ON THE LIMITING POLARIZATION OF LUMINESCENCE OF COMPLEX MOLECULES

G. P. Gurinovich, A. M. Sarzhevskii, and A. N. Sevchenko

Received 21 March 1959

In connection with the previously observed dependence of the degree of polarization of the luminescence of complex molecules on the wavelength of absorption and emission, the limiting degree of polarization of the fluorescence of solid solutions of derivatives of phthalimide in polymethylmethacrylate has been investigated. It was established that for $\nu_{exc.} = \nu_{emiss.} = \nu_{el.}$ the limiting degree of polarization P_0 for all the investigated compounds closely approaches the theoretical value of 50%. In all cases the dependence of $P_0 = f(\nu_{emiss.})$ has a mirror symmetry relative to the frequency of the purely electronic transition dependence, $P_0 = f(\nu_{exc.})$.

It was shown that the variance of values of P_0 reported in the literature, and the divergence of P_0 from the theoretical value may be explained by the effect of oscillations in the ground state and the excited states of the molecule.

INTRODUCTION

The theory of the polarized fluorescence of complex molecules, proceeding from the assumption of completely anisotropic linear oscillators for absorption and emission, leads in the case of isotropic solutions to a maximum value of limiting polarization P_0, equal to 0.5. Experimentally, this value of limiting polarization is never achieved. Since the limiting polarization is considerably different from $P_0 = 0.5$ even in solid solutions where the molecules are rigidly bound and cannot perform Brownian turning motion, the source of the phenomenon must be sought for in the intramolecular properties of the material.

The radical difference of the limiting degree of polarization from the theoretical value can be explained in many cases by the peculiarities of the luminescing molecules and the symmetry of their structure.[1] However, even in those cases where there is no basis for the assumption of several oscillators of absorption and emission, P_0 ordinarily is considerably different from $P_0 = 0.5$.

The first attempt to explain the difference of experimental and theoretical values of the limiting polarization was carried out by Perrin,[2] who for this purpose introduced the idea of elliptical oscillators. However, the ellipticity of the fluorescence of the complex molecules could not be observed. Somewhat later Yablonskii[3] made an attempt to formally describe the phenomenon by use of a three-dimensional oscillator having definite components along three axes rigidly connected with the molecule. In this fashion the possibility was demonstrated of describing all the features of limiting polarization experimentally observed. Recently Laffite[4] examined the polarization of the fluorescence of dyes from the point of view of the "metallic" model of the molecule. The presence of several short chains of conjugate bonds joining auxochrome groups in the molecules considered permitted the author to explain the departure of the limiting degree of polarization from the theoretical value. Yablonskii[5] considers that this is a particular case of the three-dimensional oscillator (the plane oscillator).

Considering the question of the limiting polarization of the fluorescence of complex molecules, it is ordinarily considered that the long wavelength absorption band and the emission band behave in the same fashion in relation to polarization; that is, that polarization does not change with the spectrum. However this situation is not clearly true.

In 1924, Levshin[6] had already observed some decrease in the degree of polarization corresponding to the degree of increase of the exciting quantum in the long wavelength limit of the absorption band. Subsequently in almost all luminescent dyes examined, analogous decreases in the degree of polarization were observed.[7] This phenomenon may be explained by the effect of oscillation of the molecule.[8] Actually if, in the case of diatomic molecules, stretching oscillations occurring along the axis of the molecule do not change the symmetry state of the molecule, and therefore have no effect on the polarization of the luminescence, in the case of complex molecules, deformation oscillations may, in a substantial manner, deform the configuration of the molecule and thus affect the polarization of the fluorescence. In this case the absorption band cannot be related to one particular direction of a linear oscillator, but rather one is forced to consider a ray with a greater or smaller spread in direction of polarization.

Measurement of the degree of polarization as a function of the spectrum of the fluorescence led Vavilov[9] to the conclusion that polarization, within the limits of experimental accuracy, does not depend on the wavelength of the fluorescence. However, later[10] such a dependence was observed in more rigorous conditions of the experiment (excitation by monochromatic light, broad interval of spectra investigated, and higher precision of measurements). In connection with this, it would be interesting to attempt to obtain the theoretically expected degree of polarization in case all depolarization factors were removed.

EXPERIMENTAL

For obtaining the limiting value of the degree of polarization it is necessary to exclude the influence of Brownian rotational movement of the molecule on the polarization of the fluorescence. This can be accom-

plished by two means: first, one may take account of the turning of the molecule with time in the excited state, as is ordinarily done by an extrapolation to infinite viscosity, in conformity with the Levshin-Perren formula; secondly, one may immobilize the molecule, setting it into a solid medium. The first method is linked with systematic errors related with the fact that micro- and macro-viscosity are not the same; therefore it is necessary, when possible, to resort to the second course. Both methods are used in this paper.

As a solid solvent, polymethylmethacrylate (plexiglass) was used. Derivatives of phthalimide (3-monomethylaminophthalimide, 3-monomethylamino-N-methylphthalimide, 3-aminophthalimide, 3-amino-N-methylphthalimide, and 3.6-diamino-N-methylphthalimide) were dissolved in monomethylmethacrylate, and in special glass forms were polymerized after addition of 1-2% polymerization initiator (benzoyl peroxide) in a water bath at 50-70°C. From the solid solution obtained as a result of the polymerization, squares were cut out, from which, after grinding and polishing, homogeneous, completely transparent samples, suitable for polarization measurements, were obtained. In order to avoid concentration depolarization, all samples were prepared with a concentration of $C = 5 \times 10^{-6}$ gm/cm³. For measurement of absorption spectra, the concentration was increased to the necessary degree.

One should note that although methylmethacrylate does not in itself have any noticeable double refraction, because of internal stresses, none of the samples was completely isotropic. This may reduce somewhat the value of measured polarization; however, as the experiments show, errors from this cause are negligible. As a control in the polarization measurements, observations were made at two positions on each sample. Differences in the values obtained did not exceed 2% in polarization. As a viscous solvent, glycerine was used, the viscosity of which was varied over a considerable range by change of temperature. Measurement of the spectra of absorption were carried out by use of an SF-4 spectrophotometer; the fluorescence spectra were recorded by a diffraction light intensity monochromater and automatic recorder. The polarization was measured on a setup described in reference 10. The precision of the polarization measurements may be set at 3-5% of the measured quantities.

RESULTS

Changes in the degree of polarization with the absorption and emission spectra for different compounds are presented in Figs. 1-3. For clarity, in addition to the dependence of the degree of polarization on frequency of absorption and emission, emission spectra and the long wavelength absorption band are also shown. Measurement of the degree of polarization of fluorescence for the frequency corresponding to the frequency of the purely electronic transision $\nu_{exc.} = \nu_{el.}$, and excited in different parts of the long wavelength absorption band, lead to the relations shown in these figures by the straight line 1. On the other hand, for excitation by light by the frequency of the pure electron transition and measurements on the fluorescence spectrum we obtain the straight line 2. Also, in Figs. 1 and 3 are shown the dependence of the degree of polarization P_0 on $\nu_{exc.}$ for the observed fluorescence with frequency $\nu_3 < \nu_{el.}$ (straight line 3) and the dependence of the degree of polarization on $\nu_{emiss.}$ for excitation by frequencies $\nu_1 > \nu_{el.}$ (straight line 4) and $\nu_2 < \nu_{el.}$ (straight line 5). On the basis of the experimental data, one must apparently consider the dependence $P_0 = f(\nu_{emiss.})$ and $P_0 = f(\nu_{exc.})$ as linear.

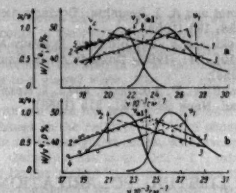


Fig. 1. Dependence of $P_0 = f(\nu_{emiss.})$ (2, 4, 5) and $P_0 = f(\nu_{exc.})$ (1, 3) for 3-monomethylaminophthalimide (a) and 3-aminophthalimide (b) in plexiglas, for different conditions of excitation and observation. Straight lines are designated as follows: 1 for $\nu_{emiss.} = \nu_{el.}$; 2 for $\nu_{exc.} = \nu_{el.}$; 3 for $\nu_{emiss.} < \nu_{el.}$; 4 for $\nu_{exc.} > \nu_{el.}$; 5 for $\nu_{exc.} < \nu_{el.}$.

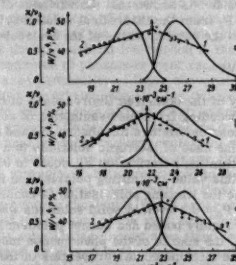


Fig. 2. Dependence of $P_0 = f(\nu_{emiss.})$ (2) and $P_0 = f(\nu_{exc.})$ (1) for 3-amino-N-methylphthalimide (a), 3,6-diamino-N-methylphthalimide (b), and 3-monomethylamino-N-methylphthalimide (c), in plexiglass, for different conditions of excitation and observation. Straight lines are designed at follows: 1 for $\nu_{emiss.} = \nu_{el.}$; 2 for $\nu_{exc.} = \nu_{el.}$.

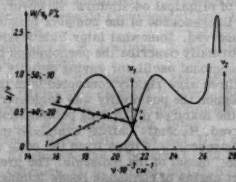


Fig. 3. Dependence of $P_0 = f(\nu_{emiss.})$ for lucigenin for excitation in different absorption bands. Straight lines are designated as follows: 1 for excitation in the first absorption band $\nu_{exc.} = \nu_{el.}$ (positive value of P_0); 2 for excitation in the second absorption band (negative value of P_0).

Figure 3 shows absorption spectra and emission spectra of lucigenin in glycerin, and the dependence of the degree of polarization on $\nu_{emiss.}$ for excitation in two absorption bands having opposite signs of polarization of the fluorescence. Lucigenin was chosen as the object of investigation because it has a very intense second absorption band, which corresponds to a large negative value of polarization. Unfortunately this material is very slightly soluble in methylmethacrylate, and therefore the measurements had to be carried out in glycerine solutions, in which turning Brownian movements of the molecule take place. Consequently, the values of polarization obtained are considerably less than might have been expected in polymethylmethacrylate. As is evident from the figures presented, the absolute value of the degree of polarization increases considerably in proportion to the nearness to the frequency of the purely electron transition, both for positive and also for negative values of the degree of polarization. In a majority of the cases, the dependence $P_0 = f(\nu_{emiss.})$ put in the frequency scale, has a mirror symmetry with the dependence $P_0 = f(\nu_{exc.})$.

The absolute value of the degree of polarization for excitation by light with frequency corresponding to the frequency of the pure electronic transition $\nu_{el.}$, and also for observation of fluorescence at the same frequency (the point of intersection of the straight lines in Figs. 1 and 2) in solid solutions are reasonably close approximations to the theoretical limit of the value $P_0 = 0.5$; but they never lie above it. Although the selection of compounds for investigation was made with the idea that the limiting polarization, obtained by the ordinary method, is considerably different from compound to compound, the degree of polarization at the point corresponding to $\nu_{el.}$ is almost always the same. It may be presumed that within the limits of experimental precision all of the compounds studied have one and the same value of the degree of polarization, equal to 0.48. It is characteristic that for excitation in the antistokes (translator's note: I am using a direct transliteration of this term) region of the spectrum for $\nu_a < \nu_{el.}$ (Fig. 1) the dependence of the degree of polarization on $\nu_{emiss.}$ takes the same course as for $\nu_{exc.} = \nu_{el.}$.

The values of limiting degree of polarization obtained under standard conditions of experimentation (over-all observation of fluorescence, excitation through a light filter transmitting a considerable spectral range, and extrapolation to infinite viscosity by the formula of Levshin-Perrin), and the values of P_0 obtained by taking account of the dependence of P_0 on $\nu_{emiss.}$ and $\nu_{exc.}$ are presented in Table 1 (second and fifth columns). In the sixth and seventh columns of the table are presented the respective limits of change of $\Delta P_{absorp.}$ of the degree of polarization in percentages based on the absorption spectrum and emission spectrum ($\Delta P_{emiss.}$), for changes in frequency up to 6000 cm^{-1}. As is evident from these data, the degree of polarization changes approximately the same within the limits of the emission band and the long wavelength absorption band. The mean value of ΔP relative to the frequency interval of 6000 cm^{-1} exceeds 9%.

Table 1

Material	P_0 % in glycerin	P_0 % in plexiglass	P_0 % predicted	P_{el} %	$\Delta P_{absorp.}$ %	$\Delta P_{emiss.}$ %
3-monomethylamino-phthalimide	40.0	44.0	44.4	49.2	6.8	7.2
3-monomethylamino-phthalimide	40.0	—	40.5	45.0	8.5	7.9
3-monomethylamino-N-methylphthalimide	40.0	41.0	40.5	48.5	9.5	8.7
3-aminophthalimide	32.2	41.5	42.0	48.5	9.1	8.2
3-amino-N-methylphthalimide	35.0	39.0	39.5	47.4	9.2	7.4
3,6-diamino-N-methyl-phthalimide	38.0	40.0	39.5	47.7	12.2	11.9
Lucigenin ($\lambda_{exc.}$ = 474 mμ)	39.0*	—	39.0*	42.4*	—	12.4*
Lucigenin ($\lambda_{exc.}$ = 365 mμ)	−20.0*	—	−20.0*	−23.0*	—	8.0*
Fluorescein	38.0	—	38.5	42.8	8.5	8.8
Rhodamine B	40.0	—	40.5	45.4	12.4	18.4

*The values of the degree of polarization in glycerine at room temperature were obtained without extrapolation to infinite viscosity.

From the data presented in Figs. 1 and 2 it is easy to predict the results of measuring the degree of polarization under ordinary conditions of experimentation (over-all observation of fluorescence, excitation through a light filter). If it be assumed that in the first approximation $\nu_{exc.}$ corresponds to the maximum of the long wavelength absorption band, and the measured polarizations correspond to $\nu_{emiss.}$, equal to the frequency of the maximum of the fluorescence band, in order to obtain the value of the degree of polarization expected under ordinary conditions of experimentation, it is sufficient to draw a straight line parallel to the straight line corresponding to $P_0 = (\nu_{emiss.})$, through a point the abscissa of which is equal to the frequency of the maximum of the absorption band, and the ordinate equal to P_0 for the purely electronic excitation and emission. The value of the degree of polarization corresponding to the maximum of the fluorescence band will also be the sought-for quantity. The values obtained in this manner are shown in the fourth column of Table 1, and the results of the experiment in the third. As is evident from these data, discrepancies do not exceed 1%.

CONSIDERATION OF RESULTS

All the experimental results obtained can be explained if one assumes that the degree of polarization depends on oscillations in the molecule both in the ground state, and in the excited states. Actually, from the point of view of quantum mechanics the property of polarization of the fluorescence depends on component matrix elements of the transition between the levels m and n in

$$D_{mn} = \int \psi_m^* D \psi_n d\tau$$

certain component directions in the molecule. These components of the matrix element of transition in turn are determined by the symmetry properties of the combining states. If the transition on absorption takes place between oscillating sublevels of the ground and excited states of the molecule (transition 1, Fig. 4), and transition with emission of fluorescent light between the same oscillation sublevels, (transition 1'), the polarization should be determined only by the properties of the matrix element of the transition. If the matrix element of the transition has only one component different from zero (the linear oscillator), the measured degree of polarization when depolarization sources are removed

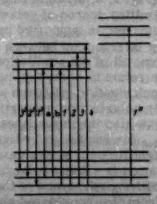


Fig. 4. Transition scheme between oscillation sublevels of the ground and excited electronic states.

should be equal to 0.5. Actually, for excitation of the fluorescence by light with frequency $\nu_{el.}$ and measurement of the degree of polarization of fluorescence of the same frequency $\nu_{el.}$ we observed maximum values, close to 0.5. Some of the difference on the lower side from the theoretically possible value (0.48 in place of 0.5) can be traced to the following depolarizing factors: first, there will always be (even in solid solutions) oscillations of the entire molecule; secondly, in measuring the degree of polarization even by use of a monochromator, we have to deal not with a single frequency, but with a spectral interval of frequencies; thirdly, even with completely monochromatic light we observe transitions of one frequency, but transitions occur between different pairs of combining oscillation sublevels (arrow 1 and B). Further, all the factors connected with imperfection of the experiment (nonparallel light beams, inhomogeneity of the samples, lack of precision in the orientation of the polarizer, etc.), lead ordinarily to a decrease in the measured degree of polarization of the light. Thus in the ideal case (arrows 1 and 1′) we should observe a degree of polarization equal to 0.5; that is, transition between two combining levels is completely anisotropic, and have only one component of the matrix element of transition.

If the degree of polarization of fluorescence is measured from the frequency $\nu_{el.}$ (arrow 1′), and excitation is effected by different frequencies (arrows 1, 2, 3, ...), the degree of polarization should be decreased according to the degree of increase of excited quanta, in the case where the matrix element of transitions 2 and 3 have a component different from zero in a direction forming some angle with the direction of the dipole moment of the transition 1′ with emission. Since such a decrease in the degree of polarization is actually observed, the presence of the designated angle may be considered to be proven. Conversely, if excitation is effected by monochromatic light of frequency $\nu_{exc.} = \nu_{el.}$, and the degree of polarization is measured in different parts of the spectrum of fluorescence (arrows 1′, 2′, 3′, ...), for the same reason, a decrease in the degree of polarization in the fluorescence spectrum should be observed. In the case where excitation is carried out through a light filter, and P is measured in the spectrum of fluorescence as a function of frequency, or on the other hand, the degree of polarization of the entire fluorescence band is measured, and excitation is carried out in different parts of the long wavelength absorption band, then as can be easily seen from Fig. 4, a less noticeable dependence of the degree of polarization should be observed on the wavelength of the fluorescence or absorption respectively. It follows from the same Fig. 4 that on excitation by frequency $\nu_{exc.} = \nu_{el.}$ (arrow a) the course of the dependence of the degree of polarization on the spectrum of fluorescence should be the same as for excitation by frequency $\nu_{exc.} = \nu_{el.}$. Actually, this is also observed in the experiments (Fig. 1, a, straight line 5). The dependence of the limiting degree of polarization on $\nu_{em.}$ and $\nu_{exc.}$, as considered, is supported by the fact that in spite of the strong interactions between the oscillation degrees of freedom, all of the oscillation levels of a complex molecule retain to some degree their individuality, indicated by polarization, although also strong neutralization of their polarization properties takes place.

Figure 1 shows also the dependence of the degree of polarization on $\nu_{em.}$ for excitation by light with frequency $\nu_{exc.} > \nu_{el.}$ (straight line 4). In this case, the measured degree of polarization is substantially less than in the case $\nu_{exc.} = \nu_{el.}$ although the trend of the dependence is hardly different from that considered above. It is characteristic that for extrapolation of the line 4 to intersection with the abscissa $\nu = \nu_{exc.}$ the absolute value of

Fig. 5. On the question of the influence on the degree of polarization of the angle between the oscillators responsible for absorption and emission.

the degree of polarization reaches the value P_0, measured for $\nu_{exc.} = \nu_{el.}$. This can be easily explained as shown in Fig. 5. Actually, the direction of the dipole moment of the transition with absorption of light 1 can have a considerably larger angle with the direction of the dipole moments of the transition with emission 3′, 4′, ..., than in the case of excitation by frequency $\nu_{exc.} = \nu_{el.}$, and it would follow that the degree of polarization of the fluorescence should be lower, which was observed in the experiment. If one should observe fluorescence of a frequency corresponding to the arrow 1′, we would have the case of oscillators coinciding in their direction, and the degree of polarization would be close to 0.5. Extrapolation of the dependence $P_0 = f(\nu_{em.})$ up to the intersection with the line corresponding to $\nu = \nu_{exc.}$, goes through the same value. Analogous regularity is observed also in the case $P_0 = f(\nu_{exc.})$ and $\nu_{em.} < \nu_{el.}$ (line 3).

Especially interesting is the case where excitation is carried out in the second absorption band (Fig. 3), which corresponds to negative values of the degree of polarization. In this case, as was said already, the same observations were made of the dependence of the degree of polarization on $\nu_{em.}$ (line 2), in which the absolute value of P increases proportionately with increase of $\nu_{em.}$. This fact is also easily explained, if one keeps in mind that a negative value of the degree of polarization corresponds to oscillators of absorption and emission forming an angle close to $\pi/2$. In this case the directions of the dipole moments of the transitions 1′, 2′, 3′, ... (Fig. 4) would form with the direction of the dipole moment transition with absorption, an angle different from $\pi/2$, which also leads to a decrease of the absolute value of the degree of polarization.

Thus in all cases of a transition with emission to a higher oscillation sublevel of a lower electronic state for monochromatic excitation a decreased polarization of the emitted light is the result. Only for $P_0 = 0$ a dependence of the degree of polarization on $\nu_{em.}$ cannot in principle be observed.

As has been stated in reference 10, when the rule of mirror symmetry of spectra is established,[11] that is, when the wave functions characterizing the oscillation sublevels of the lower and upper electronic states are equal for similar amounts of oscillation energy[12]

$$\psi_{osc.}(E_{osc.}) = \psi^*_{osc.}(E^*_{osc.}) \quad \text{for} \quad E_{osc.} = E^*_{osc.},$$

in relation to the dependence of the degree of polarization on $\nu_{em.}$ and $\nu_{exc.}$, the rule of mirror symmetry should also be valid. In all the cases presented, this rule is established experimentally, departures not exceeding experimental error.

A formula obtained by Levshin,[13] Perrin,[14] and later

TABLE 2

Material	Solvent	$P_{0\,max}$ %	b_1	γ_1	$P_{0\,min}$ %	b_2	γ_2	$\gamma = \gamma_2 - \gamma_1$
3-aminophthalimide	Plexiglas	48.5	0.012	6°30'	40.3	0.078	16°30'	10°00'
3-amino-N-methylphthalimide	Plexiglas	47.4	0.02	8°00	40.0	0.08	18°30	8°30
3-monomethylaminophthalimide	Plexiglas	48.2	0.008	4°30	42.0	0.062	14°30	10°00
3-monomethylamino-N-methylphthalimide	Plexiglas	46.5	0.028	9°30	37.8	0.096	18°00	8°30
3,6-diamino-N-methylphthalimide	Plexiglas	47.7	0.018	7°30	35.8	0.114	19°30	12°00
Lucigenin	Glycerin	42.4	0.08	14°00	30.6	0.155	23°00	9°00
Fluorescein	Glycerin	42.8	0.057	14°00	34.0	0.129	21°00	7°00
Rhodamine B	Glycerin	43.4	0.053	13°30	30.0	0.16	23°30	10°00
3-monomethylaminophthalamide	Glycerin	45.0	0.04	11°30	38.0	0.078	16°30	8°00

by Yablonskii[15]

$$P_0 = \frac{9b^2 - 12b + 4}{3b^2 - 4b + 8}$$

in conformity with which the limiting degree of polarization P_0 is connected with the mean value of the square of the sin ($b = \overline{\sin^2\gamma}$) of the angle formed by the directions of the dipoles of the moments of transitions with absorption and emission, can be used in this case for quantitative prediction of the influence of oscillations on the limiting polarization. For small b this formula is simplified to the form

$$P_0 = 0.5 - 1.25b$$

Angles between the directions of dipole moment of transitions with absorption and emission, computed according to this formula, are shown in Table 2. As is evident from this table, the maximum angle γ calculated in an interval of 6000 cm^{-1} amounts on the average for all the compounds studied to 10 deg.

These results as discussed have been appropriately established in somewhat more detail in the work of Laffite[4] and Yablonskii.[5] Laffite investigated the limiting polarization of certain dyes in plexiglas and obtained for excitation, by observation through a light filter, a value for the limiting degree of polarization of 45% for fluorescein, and 46% for rhodamine. The departure from 50% was explained, as indicated above, by the presence of several possible mechanisms of joining the auxochrome group by conjugate chain bonds. In this way the existence of the so-called plane oscillator may be established.[5] It, however, one takes into account that in the compounds studied by Laffite the dependence of the degree of polarization on the spectrum of absorption and emission was also observed,[10] then in the case $\nu_{em.} = \nu_{exc.} = \nu_{el.}$ we should obtain a value of the degree of polarization 3-4% higher than those observed, that is, practically the theoretical value of the limiting polarization P_0 for a completely anisotropic linear oscillator. Therefore, to speak of the plane oscillator in this case apparently has no meaning. One should, however, carry out a special experimental proof of this assertion.

CONCLUSIONS

1. The degree of polarization of the fluorescence of complex molecules both in viscous, and also in solid solutions depends on the frequency of the exciting light and on the frequency of the fluorescence, decreasing proportionally to the distance from the frequency of the purely electronic transition. Changes in the degree of polarization with spectra of absorption and emission amount to 10% and more.

2. The dependence of the degree of polarization on the frequency of excitation light within the limits of the long wavelength band of absorption and emission can be explained by the different orientation of dipole moments of the direct and reversed transitions.

3. For all the compounds studied the limiting degree of polarization measured for $\nu_{exc.} = \nu_{em.} = \nu_{el.}$, was very closely approximated by the theoretical limiting value of 50%. Transition with emission and absorption between one and the same pair of levels is apparently completely anisotropic and can be described in terms of a linear oscillator model. Introduction of the idea of three-dimensional and plane oscillators in this case cannot be justified. The difference of the value of P_0 obtained by the usual method, from 50%, is apparently explained by the influence of oscillations on the measured polarization of fluorescence.

4. For the realization of the rule of mirror symmetry in the spectra, the dependence of P_0 on the frequency of the exciting light within the limits of the long wavelength absorption band has a mirror symmetry relative to $\nu_{el.}$ of the dependence of P_0 on the emission frequency. This fact is another example of the rule of mirror symmetry.

REFERENCES

1. P. P. Feofilov. Doklady Akad. Nauk SSSR 87, 343 (1947).
2. F. Perrin. J. de Phys. 7, 390 (1926).
3. A. Jablonski. Z. Phys. 96, 236 (1935).
4. E. Laffite. Ann. phys. 10, 71 (1955); J. phys. radium, 15, 37 (1954).
5. A. Jablonski. Nuovo cimento 5, 995 (1955).
6. V. L. Levshin. Zhur. Russ. Fiz. Khim. Obshchestva, Ch. Fizich., 56, 235 (1924).
7. P. P. Feofilov. Uspekhi Fiz. Nauk 34, 417 (1948).
8. P. P. Feofilov. Dokt. diss., GOI, 1955.
9. S. I. Vavilov, Sbornik soch. 1, 129, 182 (1954).
10. G. P. Gurinovich and A. N. Sevchenko. Izv. Akad. Nauk SSSR, Ser. Fiz. 11, 1407 (1958).
11. V. L. Levshin. "Photoliuminestsentsiya tverdykh i zhidkikh veshchestv." (Photoluminescence of Solid and Liquid Materials), GITTL, 1951.
12. B. I. Stepanov. "Liuminestsentsiya slozhnykh molekul." (Luminescence of Complex Molecules), Izd. Akad. Nauk SSSR, 1955.
13. V. L. Levshin. Z. Physik 32, 307 (1925); Zhur. Russ. Fiz. Khim. Obshchestva, Ch. Fizich. 57, 283 (1925).
14. J. Perrin. Inst. Solvay, 322 (1925).
15. A. Jablonski. Acta Phys. Polon. 10, 33, (1950).

THE EFFECT OF ELASTIC DEFORMATION BY UNIAXIAL COMPRESSION AND ELONGATION OF CRYSTALS ON THE SPECTRA OF LOCAL ANISOTROPIC CENTERS IN A CUBIC LATTICE
I. METHOD

A. A. Kaplyanskii

Received 10 March 1959

It is shown that from the splitting patterns of the spectral bands of anisotropic centers in cubic crystals under uniform elastic deformation by uniaxial compression (or elongation) of the crystals, it is possible unequivocally to determine the orientation of the centers in the lattice and the nature of the elementary oscillators which describe the absorption and emission of light by the centers.

INTRODUCTION

In recent years there have been many papers devoted to the investigation of localized complex anisotropic centers in crystals of the cubic system. In the papers of Feofilov (see the survey in reference 1) anisotropic centers were experimentally detected and studied in certain cubic crystals; the general rules of their behavior were established, and a series of optical methods for studying such centers proposed. As is shown in these papers, anisotropic centers are oriented in a cubic lattice along axes of symmetry, of one order or another. Thereby, because of the equally probable distribution of the centers about the several axes of symmetry of a specific order, the micro-anisotropy of the centers is found to be averaged out and concealed in the macroscopic properties of cubic crystals connected with the presence of centers (in particular, the crystals retain optical isotropy). In order to expose the "hidden" anisotropic centers, it is necessary to show in a monocrystal some decidedly anisotropic influence which has a different effect on the groups of centers oriented along the different axes of a given order. This principle forms the basis of the proposed optical methods for determining the orientation of anisotropic centers in cubic crystals—the study of the polarized luminescence of localized centers in crystals,[2,3] the investigation of the photochemical conversion of centers in crystals under the action of polarized light,[4,5] and the study of the Zeeman splitting of the bands in the spectra of centers in cubic crystals.[6] These methods also permit the determination of the nature of the elementary oscillators corresponding to the spectral bands of the centers.[6,7]

A knowledge of the orientation of the anisotropic centers in cubic crystals and of the natures of the elementary oscillators which describe the absorption and emission of light by the centers is extremely important. The known character of the orientation allows one to propose a basic physical model of the center, and the multipole-order of the oscillators is important for the formulation of the quantum scheme of energy levels for the centers. By the use of the methods enumerated above, the anisotropy of the centers was detected experimentally and their orientation determined in some crystals.[2,4-8,8-12] The well-known limitations in the applicability of the indicated methods of investigating anisotropic centers should be noted, however. Thus, a requirement for the study of the azimuthal dependence of the degree of polarization of luminescence is the existence in the crystal of polarized luminescence, which does not occur in many systems. The possibility of investigating anisotropic photochemical conversions involves, of course, a sufficient photochemical sensitivity of the centers, absent in many cases. The study of the Zeeman effect requires narrow spectral bands, and is also limited by a number of other circumstances.[8] Hence an interest has developed in the search for new means of investigating anisotropic centers in cubic crystals which are capable of supplementing the methods already available.

THE SPLITTING OF THE SPECTRAL BANDS OF ANISOTROPIC CENTERS IN A CUBIC LATTICE BY ELASTIC DEFORMATION BY UNIAXIAL COMPRESSION AND ELONGATION OF THE CRYSTAL

As an anisotropic influence on cubic crystals, required for the exposure of hidden anisotropic centers, the utilization of uniaxial elastic compression (or elongation) of a crystal[13] seems possible. Let us consider the lattice of a cubic monocrystal submitted to a uniaxial compression* along an arbitrary direction P; we shall consider that the deformation of the crystal arising thereby is uniform and elastic. We shall assume that the localized centers of the crystal represent anisotropic formations that have been oriented along several axes of symmetry of specific order G_n ($3G_4$ or $4G_3$ or $6G_2$). Then, upon uniaxial compression of the crystal groups of centers, which are located along the 12/n different axes of the nth order, are found, in general, in different locations relative to the axis of compression P, since the axes G_n form different angles with P. Because of this, the characteristics of elastic displacement in the lattice in the region of the centers will differ for these groups of centers. Since the energy state of the centers depends essentially on their interactions with the lattice, it is natural to assume that the elastic deformation in the lattice causes some shift of the energy levels of the centers. Since the deformation in the region of the anisotropic centers differs for groups of centers which are differently disposed with respect to the axis P, the shift of the levels will be different, generally speaking, for different groups of centers. In such manner, elastic uniaxial compression of a cubic crystal, in principle, removes the "orientation degeneracy" of the energy levels of anisotropic centers oriented along several axes G_n. This concerns the ground level as well as the excited levels of the centers.

In connection with this, it should be expected that the separate spectral emission or absorption bands of the

*For brevity in this paragraph we shall speak only about uniaxial compression. In addition, all of the reasoning and conclusions are completely valid also for the case of uniaxial elongation of the crystal.

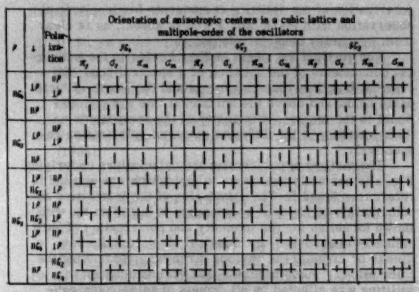


Fig. 1. Scheme for the polarized splitting of the spectral bands of anisotropic centers in a cubic lattice upon elastic uniaxial compression and tension of the crystals.

free crystal, originating from transitions between the levels of anisotropic centers, will experience a splitting in a uniaxially strained crystal. For a given orientation of the centers along the axes of nth order, the number of components of the splitting is determined by the number of different locations relative to P of those several (12/n) axes of symmetry G_n along which the centers are oriented. For the purpose of computation, it is expedient to apply the compression of the crystal along one of its symmetry axes. In this case the number of components of the splitting may be easily computed for the various directions of P ($P \parallel G_4$, $P \parallel G_3$, $P \parallel G_2$) and for the cases of orientation of the centers along axes of different order ($3G_4$, $4G_3$, $6G_2$). The results of the calculation of the number of components are presented in the table. As

P	Orientation of the centers		
	$3G_4$	$4G_3$	$6G_2$
$\parallel G_4$	2	1	2
$\parallel G_3$	1	2	2
$\parallel G_2$	2	2	3

follows, from the table, the set of numbers of components of splitting of the spectral bands of anisotropic centers, produced by compressing the crystal along the directions of the symmetry axes of different order, uniquely determines the orientation of the anisotropic centers in cubic lattices.

The above conclusions are based upon the proposition that elastic deformation by uniaxial compression of a crystal displaces only the levels of the anisotropic centers. It is necessary, however, to keep in mind that the levels of the anisotropic centers of a free crystal can possess a degeneracy, the multiplicity of which is determined in particular by the symmetry of the crystalline field in which the centers are located.[14] Elastic deformation of a crystal by uniaxial compression, by changing in some degree the symmetry of this field, can remove the degeneracy from these levels, which leads, aside from a shift, to a splitting of the levels of the individual centers, and consequently to a complication of the general splitting of the bands in the spectrum of the deformed crystal. However, we evidently can expect that the effect of splitting the degenerate levels of individual centers is extremely small, and that it is not possible to study it, inasmuch as it is difficult to presume the appearance of significant changes in the character of the symmetry of the crystalline field upon such insignificant displacements in the lattice as take place during elastic deformation. As will be seen, the results of the experiment described in reference 15 confirms this hypothesis.

As is shown in reference 1, absorption and emission of light by anisotropic centers can be described by means of elementary dipole oscillators (linear—electrical (π_z) or magnetic (π_m) and circular—electrical (σ_z) or magnetic (σ_m)), oriented in the lattice along the 12/n axes G_n corresponding to the centers. Owing to this, the emission and absorption of light by the centers, oriented along each one of the 12/n axes of nth order, is anisotropic, its intensity and state of polarization depend on the multipole-order of the oscillators and the angle between the direction of observation and the corresponding axis of symmetry. This anisotropy is completely masked in the emission and absorption by the centers of a free cubic crystal because of participation in these processes by groups of centers oriented along all 12/n axes G_n; this produces isotropy of the optical properties of the crystal. However, as was shown above, in the case of uniaxially strained crystals, the spectral bands are split, whereby the individual components of the splitting correspond to emission or absorption of groups of centers which differ in position relative to P. Therefore we can expect that the components of the splitting will in general be polarized. Thereby, for given orientations of anisotropic centers and the direction of the axis of compression P, both the degree of polarization of the components of the splitting and their relative intensity should depend on the nature of the elementary oscillators and the direction of observation L.

Figure 1 presents schematically the results of a calculation of the relative intensities and polarization of the components of the splitting of spectral bands of the centers in a uniaxially deformed cubic crystal, for various orientations of the anisotropic centers ($3G_4$, $4G_3$, $6G_2$), directions of the axis of compression ($P \parallel G_4$, $P \parallel G_3$, $P \parallel G_2$), multipole-order of the oscillators (π_z, σ_z, π_m, σ_m), and directions of observation L. The calculation was made both for transverse ($L \perp P$), and longitudinal ($L \parallel P$) directions of observation. In the first case, the patterns of splitting are given for light polarized along the axis of compression ($E \parallel P$) and perpendicular to it ($E \perp P$). The patterns for transverse observation with $P \parallel G_4$ and $P \parallel G_3$ are the same—as follows from symmetry considerations—for an arbitrary direction $L \perp P$; for the case $P \parallel G_3$, however, where the pattern of splitting depends on the direction of transverse observation, the calculation is made for observation along the three axes of symmetry G_4, G_3, G_2, perpendicular to the axis G_3 along which the compression is directed. For longitudinal observation with $P \parallel G_3$, the pattern of the splitting is given in two mutually perpendicular directions of polarization along the axes of symmetry normal to the compression axis ($E \parallel G_2$, $E \parallel G_4$);

polarization of the splitting components for longitudinal observation with $P \parallel G_4$ and $P \parallel G_3$ is absent, as is clear from symmetry considerations.

The vertical segments in Fig. 1 refer to the individual components of the splitting of a spectral band; the over-all length of these segments and the length of their parts below and above the horizontal line are proportional to the integrated intensity of the components and their intensity in the different states of polarization respectively.

The method of performing the calculations underlying Fig. 1 is perfectly analogous to that which was applied in references 3 and 6. The calculation of the intensities and polarization of the split components is based on the well-known formulas for the intensity and polarization of light emitted (or absorbed) by classical electrical dipoles (linear or circular) in various directions. In making the calculation, it was presumed that each component of splitting was affected by all groups of anisotropic centers distributed along axes G_n making the same angle with P. In Fig. 1 the components of splitting are arranged from left to right in order of increasing value of the angles which the axes of orientation of the groups of centers corresponding to the components form with P; the distances between the components are arbitrary. The calculation was worked through for linear and circular electrical oscillators (π_e, σ_e). The pattern for the magnetic oscillators (π_m, σ_m) was obtained by a simple inversion of the state of polarization in the pattern for the corresponding electrical dipoles.

The results of the calculation cited in Fig. 1 are correct for absorption bands, and also for luminescence bands when the emission probability is the same for all anisotropic centers (isotropic excitation). Such isotropic excitation of luminescence always takes place when the acts of absorption and emission are independent and distinct, because of semiconductivity processes, for example. As for the case when absorption and emission take place within one anisotropic center,* then, under the usual conditions of exciting luminescence (by a directed nonpolarized beam of light) groups of centers which are differently oriented with respect to the beam have a different probability of absorption and, consequently, a different probability of excitation of luminescence—a fact which is necessary to take into account in the calculation of the splitting pattern. This can be done without difficulty (by means of a calculation of the probability of absorption of light by groups of centers located along the different axes of one order), for different conditions of orientation of the centers, for types of absorbing oscillators (π, σ) and for directions of the beam of nonpolarized exciting light. As an example, we show in Fig. 2 the schematic pattern of splitting of bands of luminescence of anisotropic centers for one such condition. On comparing Fig. 2 with the corresponding section of Fig. 1, it is seen that the presence of polarized luminescence in a crystal can lead to substantial changes in the relative intensity of the components of polarized splitting of the luminescence bands of a deformed crystal, compared to isotropic excitation of luminescence. The presence of polarized luminescence of centers also causes the appearance of a dependence of the splitting pattern on the direction of observation for $L \perp P$ and for the cases $P \parallel G_4$ and $P \parallel G_3$.

As is seen in Figs. 1 and 2, the splitting patterns in polarized light of the bands of anisotropic centers for different directions of compression and different conditions of observation depend very strongly on the orientation of the centers and the multipole-order of the oscillators. This specificity of the splitting theoretically allows us to determine unequivocally the orientation of the anisotropic centers in cubic crystals ($3G_4$, $4G_3$, $6G_2$) and the multipole-order of the oscillators corresponding to the bands (π_e, σ_e, π_m, σ_m) by means of the splitting pattern of spectral bands of centers in polarized light during uniaxial compression of the crystal. Moreover, as follows from Fig. 1, for an unequivocal determination it is not necessary to investigate the band-splitting for the many possible directions of compression and observation. In particular, it is seen that longitudinal observation does not give any essentially new information not obtained by transverse observation. The most specific pattern occurs upon compression along G_2 and transverse observation along two axes G_2 and G_4, normal to $P \parallel G_2$. The results of such observations are, generally speaking, sufficient for a unique determination of the orientation of the centers and the multipole-order of the oscillators. In addition, as a control one can investigate the splitting for $P \parallel G_4$.

The conclusions made above indicate only the principal possibility for studying the influence of the elastic deformation by uniaxial compression on the spectra of crystals as a method of investigating anisotropic centers in cubic crystals. The practical possibility of applying this method depends first of all on obtaining sufficient resolution of the structure of the split bands in the deformed crystal.* Consequently, the centers being studied ought to possess fairly sharp spectral bands and have a system of levels which are fairly sensitive to small electric deformations of the crystal lattice. Besides, it is necessary that the magnitude of the displacement of the levels should depend essentially on the orientation of the centers relative to P and that the shift be different for the ground and the excited states. Unfortunately, the theoretical estimates of the magnitudes of the band-splitting of anisotropic centers in a uniaxially stressed crystal are not feasible. Some preliminary estimates of the "sensitivity" of the bands to deformation may be obtained only from experimental results: by the temperature shift of bands, their shift by pressure from all sides, and also by changes in location of the bands of the cen-

L	Polarization	Multipole-order of the oscillators			
		π_e	σ_e	π_m	σ_m
$\parallel G_2$	$\parallel P$				
	$\perp P$				
$\parallel G_3$	$\parallel P$				
	$\perp P$				
$\parallel G_4$	$\parallel P$				
	$\perp P$				

Fig. 2. Splitting of the spectral bands of anisotropic centers in a cubic lattice during elastic uniaxial compression and tension of the crystals (case of polarized luminescence). The centers are oriented along $4G_3$; $P \parallel G_2$; $L \perp P$; absorbing oscillators—linear; exciting beam parallel to L.

*This circumstance requires the existence of polarized luminescence of cubic crystals and the phenomena of "spontaneous" polarization of luminescence and azimuthal dependence of the degree of polarization of luminescence which are characteristic of it.[1]

*Because of the strongly expressed dependence of the patterns of polarized splitting on the orientation of the centers and the multipole-order of the oscillators, their determination can be carried out in certain cases even in the presence of incomplete resolution of the structure of the splitting, by the observation of the phenomenon in polarized light during compression along several directions.

ters of a given type in a series of crystallo-chemically related crystals.

The requirement of sufficient narrowness of the spectral bands of centers and the lack of a theoretical estimate of their sensitivity to deformation limits the application of the method presented. Another kind of limitation is connected with the definite requirements on the mechanical properties of the crystals to allow the creation of sufficient elastic distortion in the samples. Therefore the practical possibility of investigating anisotropic centers in cubic crystals by the method indicated can be established in each concrete case only by experimental means.* The experimental investigations conducted by us on the effect of uniaxial compression on the spectra of localized centers of some cubic crystals permitted us in a number of cases to determine the orientation of the anisotropic centers in the lattice and the multipole-order of the oscillators for the spectral lines of the centers; these results will be presented in the following communication.[15]

*It is interesting to note the great possibility of investigating the influence of uniaxial deformation of cubic crystals along different crystallographic directions on a wide variety of physical properties of crystals. Thus, for example, the study of the influence of such types of deformation on electrical and galvanomagnetic properties of semiconductors can give important information about the structure of zones, processes of scattering of carriers, etc. (see reference 16 and references therein).

REFERENCES

1. P. P. Feofilov. Uspekhi Fiz. Nauk 58, 69 (1956).
2. P. P. Feofilov. Doklady Akad. Nauk SSSR 92, 545, 743 (1953).
3. P. P. Feofilov. J. Exptl. Theoret. Phys. (USSR) 26, 609 (1954).
4. M. Ueta. J. Phys. Soc. Japan 7, 107 (1952).
5. P. P. Feofilov. Doklady Akad. Nauk SSSR 98, 949 (1954).
6. V. A. Arkhangel'skaya and P. P. Feofilov. Opt. i Spektr. 4, 602 (1958).
7. P. P. Feofilov. Opt. i Spektr. 1, 131 (1956).
8. P. P. Feofilov. Doklady Akad. Nauk SSSR 99, 731, 975 (1954).
9. C. V. Doorn and Y. Haven. Phys. Rev. 100, 753 (1955); Philips Res. Repts. 12, 309 (1957).
10. J. Lambe and W. Compton. Phys. Rev. 106, 684 (1957).
11. P. P. Feofilov. Opt. i Spektr. 1, 952 (1956).
12. L. I. Tarosova and P. P. Feofilov. Opt. i Spektr. 4, 696 (1958).
13. A. A. Kaplyanskii, Materialy VII Soveshch. po liuminestsentsii, Moscow, 1958. (Proceedings of the 7th Conference on Luminescence, Moscow, 1958).
14. M. A El'yashevich. "Spektry redkikh zemel'." (Spectra of the Rare Earths), GITTL, Moscow, 1953.
15. A. A. Kaplyanskii. Opt. i Spektr. 7, 683 (1959).
16. G. E. Pikus, G. L. Bir, Fiz. Tverkogo Tela 1, 154 (1959).

THE EFFECT OF ELASTIC DEFORMATION BY UNIAXIAL COMPRESSION AND EXTENTION OF CRYSTALS ON THE SPECTRA OF LOCAL ANISOTROPIC CENTERS IN A CUBIC LATTICE
II. EXPERIMENTAL PART

A. A. Kaplyanskii

Received 10 March 1959

Reversible splitting of a number of lines into several components has been detected in the spectra of the line luminescence of the cubic crystals $CaF_2:Eu^{+++}$, $CaF_2:Sm^{+++}$ and colored LiF when these crystals were subjected to uniaxial elastic compression. From a comparison of the experimental splitting patterns with the calculated ones, the orientations of the aniosotropic centers of line luminescence in these crystals and the multipole-order of the elementary emitters are obtained for a number of spectral lines.

In our preceding communication[1]* it was shown that elastic deformation of cubic crystals by uniaxial compression (or tension) in principle should cause a splitting of the spectral bands belonging to local anisotropic centers in the crystal. In addition, the splitting patterns in polarized light obtained by deforming the crystal along the directions of its symmetry axes uniquely determine the orientation of the anisotropic centers in the cubic lattice and the multipole-order of the elementary oscillators corresponding to the spectral bands. In the present paper, we report the results of an experimental investigation of the effect of elastic deformation by uniaxial compression of some crystals of the cubic system on the spectra of their local centers.*

*Henceforth this will be designated as I. All symbols adopted in I will also be kept.

*Among the experimental works in the literature on the effect of elastic deformation of crystals on their electronic spectra, the majority have to do with isotropic compression of the crystals by hydrostatic pressure (see reference 2 and references therein, and also reference 3). Recently papers[4,5] have reported a large effect on the narrow band spectra of certain crystals (CdS, CdSe, molecular crystals), due to another type of elastic deformation, evoked by thermal stresses in cooled, rigidly-held samples (planar tension), and also by unidirectional compression of crystals. This effect appears as a shift and, sometimes, as a splitting of the lines, and as a change of intensity in the spectra of the strained samples.

EXPERIMENTAL METHOD

As objects for experimental investigation we chose crystals of cubic symmetry with local centers of absorption and luminescence, the spectra of which possess narrow lines in the visible region. This group includes

crystals of fluorite activated by rare earths, CaF_2:RE*

*The author makes use of this opportunity to express sincere thanks to P. P. Feofilov for the gift of the crystals of CaF_2:RE for investigation, for information about them, and for the interest shown towards the present work.

and colored crystals of lithium fluoride, LiF. The effect of elastic deformation (uniaxial compression) of the crystals on their absorption and emission spectra was studied in polarized light by transverse observation (perpendicular to the axis of compression). For this, the crystals were cooled to the temperature of liquid nitrogen (T = 77°K). The schematic arrangement for investigating the luminescence spectra is presented in Fig. 1. The apparatus for observing absorption spectra differs from this by the replacement of the mercury lamp and filter with an incandescent lamp.

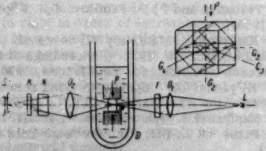


Fig. 1. Schematic arrangement for investigating the effect of uniaxial compression of a crystal on the luminescence spectrum. L—mercury lamp SVDSh-1000; O_1—quartz objective; F—filter UFS-1; M—sample; P—press; D—quartz Dewar with liquid nitrogen; O_2—glass objective; N—birefringent crystal of Iceland spar; K—quarter-wave plate; S—spectrograph slit (ISP-51 with auto-collimating camera, f = 1300 mm). Upper right—distribution of crystallographic symmetry axes of the sample with $P \parallel G_2$.

The samples for investigation were cut out of monocrystalline blocks by splitting along cleavage planes: the (111) plane in CaF_2:RE, and the (100) plane in LiF. The samples were in the shape of elongated rectangular prisms; the two faces of the prisms to which the compressive force was applied were parallel to crystallographic planes of the cube: i.e., the (100) plane, for investigation of compression along G_1, and any of the rhombododecahedral planes (110) for investigation of compression along G_2. Figure 1 also shows the distribution of the symmetry axes of the crystal in the sample for $P \parallel G_2$, when transverse observation takes place along several directions ($L \parallel G_2$, $L \parallel G_3$, $L \parallel G_4$). (This is done by turning the sample in the press around the vertical axis of compression P.)

RESULTS OF INVESTIGATION OF THE EFFECT OF UNIAXIAL COMPRESSION ON THE SPECTRA OF FLUORITE CRYSTALS ACTIVATED WITH RARE EARTHS

The spectra of trivalent ions RE^{+++} introduced into the lattice of CaF_2 were examined. The possibility of anisotropic centers of absorption and emission in this case is connected with the asymmetry in the immediate surroundings of the RE^{+++} ion, which replaced Ca^{++} in the CaF_2 lattice.[5]

A study was made of the effect of uniaxial compression on the absorption spectra of crystals of CaF_2 containing Ho, Pr, Nd, and Er, and on the luminescence spectra of CaF_2 with Er, Sm, and Eu. It was shown that the effect of compression ($P \parallel G_2$) on the spectra of crystals of CaF_2 with Ho, Er, Nd, and Pr is small. In these crystals some displacement and broadening of the spectral lines was caused by deformation, but the splitting necessary for comparison with calculation was not observed. At the same time, a well-defined polarized splitting of several luminescence lines was observed in deformed CaF_2 crystals containing Eu and Sm, permitting comparison with the calculated data (I).

1. CaF_2:Eu^{+++}. The effect of a uniaxial compression of the crystals on the luminescence spectra of type I was examined.[6] At 77°K this spectrum consists of a large number of narrow lines of different intensities, located chiefly in the yellow and red regions of the spectrum.[6,7] The anisotropic character and orientation of the emitting centers of these crystals is known from studies of polarized luminescence and the Zeeman effect.[7,8]

We have established that compression along G_2 brings about a doublet splitting of three short wavelength lines of the luminescence spectrum—λ5282 A, λ5735 A, λ5808 A (Fig. 2). The magnitude of the splitting is about the same for the different lines and, for example, is equal to 2.5 cm^{-1} for a uniaxial compression of p = 20 kg/mm^2 (λ5808 A). All three doublets are polarized; the relative intensity and degree of polarization of their components depend essentially on the direction ($L \parallel G_4$, $L \parallel G_3$, $L \parallel G_2$) of transverse observation (Fig. 2). In the doublet λ5735 A, only the short wavelength constituent is seen in the $E \parallel P$ component of polarization, whereas both constituents are observed in the $E \perp P$ component. The

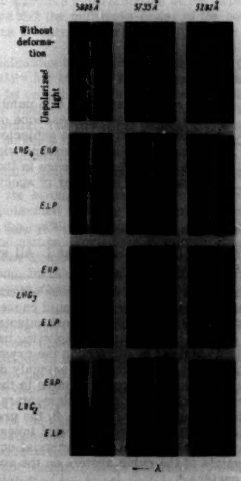


Fig. 2. Splitting of the luminescence lines of CaF_2:Eu^{+++} upon compression of the crystal along a symmetry axis of second order.

relative intensities of these components change rapidly with a 90 deg change in the direction of observation (Fig. 1a)—from $L \parallel G_3$ to $L \parallel G_4$ (where only one long wavelength constituent is observed). The polarization of the doublet λ5282 A is completely analogous to λ5735 A. At the same time the polarization of the doublet at λ5808 A is completely different; here one always sees both components of the doublet in both the $E \parallel P$ and the $E \perp P$ components, and their relative intensities change sharply when the direction of observation is changed.

For compression of the crystal along G_4, no splitting of the lines λ5808 A, λ5735 A, and λ5282 A was observed; only a slight shift of the lines took place.

The absence of splitting of the lines for $P \parallel G_4$ and the doublet splitting for $P \parallel G_3$ indicated (I, table) an orientation of the corresponding anisotropic centers along $4G_3$. The splitting pattern obtained and the relative intensities of the components of the doublets for $P \parallel G_3$ and for different conditions of observation show a complete qualitative correspondence with the results of the calculation (I, Fig. 2) of splitting for the centers oriented along $4G_3$ (oscillators π_z for λ5735 A and λ5282 A, σ_m for λ5808 A), and for the presence of polarized luminescence with absorbing π-oscillators, such as actually occur in $CaF_2:Cu^{++}$.[7] The results of the determination of the orientation of emitting centers in $CaF_2:Eu^{+++}$ obtained here and the multipole-order of the oscillators for the lines agree, on the whole, with the determinations performed previously by other methods.[7,8] This agreement can be considered as a confirmation of the theoretical premises (I) of the present method of investigating anisotropic centers in cubic crystals.

It should be noted that the line λ5735 A belonging to a transition in Eu^{+++} between levels with $I = 0$ ($^7F_0 - {}^5D_0$), is a so-called "neutral" line, not being split in an external field of any symmetry.[9] Thus the splitting of λ5735 A which we have observed may appear strange, although it is clear from I that it results not from a splitting of the levels of separate ions, but from a "sorting" of ions in the uniaxially strained crystal into two groups which find themselves in somewhat different circumstances. It is interesting that an analogous simple doublet splitting is shown by both of the lines λ5282 A and λ5808 A, which correspond to transitions with the participation of degenerate levels. This implies that the splitting of levels of individual ions upon deformation of the crystal, if it takes place, is markedly less than the shifts of the levels and practically unnoticeable in the observed splitting patterns.

2. $CaF_2:Sm^{+++}$. A study was made of the effect of deformation on crystals with a luminescence spectrum of type I, which is composed of a large number of lines in the yellow and red regions of the spectrum.[6] It should be noted that existing methods of investigation have not been successful in determining the character of the centers in the lattice of $CaF_2:Sm^{+++}$, because the luminescence of the crystals is unpolarized and the magnetic splitting of the lines has an "anamalous" character, not permitting its comparison with any calculations.[9]

We have found that compression of a crystal along axis G_3 brings about a doublet splitting of two intense short wavelength luminescent lines λ5710 A and λ5720 A, with a displacement of the center of the doublet to the long wavelength side (Fig. 3). The magnitude of the splitting is less than that observed in the lines of $CaF_2:Eu^{+++}$ and is approximately 1.8 cm^{-1} for $p = 25$ kg/mm². The doublet is polarized, and the state of its polarization depends on the direction of transverse observation ($L \parallel G_4$, $L \parallel G_3$). With $L \parallel G_4$, the splitting patterns of both doublets in polarized light are completely alike (Fig. 3). In the $E \parallel P$-component of polarization,

Fig. 3. Splitting of the luminescence lines of $CaF_2:Sm^{+++}$ upon compression of the crystal along a symmetry axis of second order.

the long wavelength component of the doublet is more intense than the short-wavelength component; in the $E \perp P$-component of polarization, on the other hand, the long wavelength component of the doublet is more intense than the short wavelength one. With $L \parallel G_3$, the patterns of splitting differ for the two doublets. At λ5710 A, the pattern in the $E \parallel P$-component remains as before (as with $L \perp G_4$), but in the $E \perp P$-component, the intensities of the components of the doublet become equal. With λ5720 A, on the other hand, the pattern remains unchanged in the $E \perp P$-component, but in the $E \parallel P$-component the intensities of the components of the doublet become the same.

The doublet character of the splitting of the lines with $P \parallel G_3$ and the polarization of the doublets shows that the emitting centers in $CaF_2:Sm^{+++}$ are anisotropic; the observations completely correspond qualitatively to the calculated patterns (I, Fig. 1) of the splitting with isotropic stimulation of luminescence and orientation of centers along $4G_3$ for the cases of circular oscillators σ_e (λ5710 A) and σ_m (λ5720 A). The orientation found for the centers of luminescence in crystals of $CaF_2:Sm^{+++}$ is identical to the orientation of the centers experimentally established previously[7,8] in crystals of CaF_2 containing a number of different RE^{+++} ions (Eu, Ho, Tb, Dy) and having spectra of Type I.

RESULTS OF THE STUDY OF THE EFFECT OF UNIAXIAL COMPRESSION ON THE LINE SPECTRA OF COLORED CRYSTALS OF LITHIUM FLUORIDE

In the absorption spectra of strongly colored crystals of LiF at low temperatures narrow "atomic" lines, first observed by Pringsheim, occur along with wide absorption bands. Narrow lines have also been observed recently at 77°K in the emission spectrum of colored LiF.[11] The origin of narrow lines in the spectra of colored crystals of LiF is still completely unknown; hence there is great interest in obtaining further information about them.

Our study of the effect of uniaxial compression of

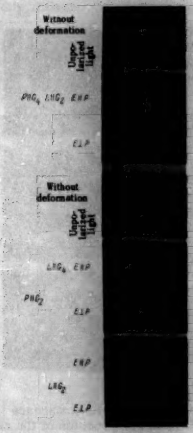


Fig. 4. Splitting of the luminescence line λ5698 A of crystals of x-rayed LiF upon compression of the crystal along symmetry axes of second and fourth order.

crystals on the luminescence spectrum of crustals of LiF which had been colored by x-rays* was essentially an

*The author is very grateful to I. N. Zimkin for carrying out the x-ray irradiation of the crystals.

investigation of the main line of the equidistant emission series λ5698 A, and also of the several neighboring irregularly distributed lines: λ5627 A, λ5830 A, and λ6246 A.[11] It was discovered that compression of the crystal along G_4 brought about a doublet splitting of the line λ5698 A (Fig. 4). The magnitude of the splitting is approximately 13 cm^{-1} for a compression of p = 15 kg/mm^2. The doublet is polarized in such a way that only its short wavelength constituent is observed in the E ∥ P component of polarization, but both of the constituents are seen in the E ⊥ P-component. Their relative intensities differ somewhat for L ∥ G_4 and L ∥ G_2.

Upon compression of the crystal along G_2 the line λ5698 A splits into a triplet. The two long wavelength components are so close together that they are poorly resolved in the spectrogram, but the short wavelength component is widely separated from them. The separation between the outer constituents of the triplet equals, for example, 25 cm^{-1} for p = 15 kg/mm^2. In the E ∥ P-component of polarization there are two short wavelength constituents of the triplet, the relative intensities of which differ somewhat for L ∥ G_4 and L ∥ G_2. In the E ⊥ P-component of polarization with L ∥ G_4, the two close long wavelength constituents of the triplet are seen, but with L ∥ G_2 only the middle constituent is observed.

The doublet splitting of λ5698 A with P ∥ G_4, the triplet splitting with P ∥ G_2, and the character of polarization of the splitting structure all correspond well with the calculated pattern (I, Fig. 2) for anisotropic centers oriented along $6G_2$ and the case of a linear electrical oscillator.* It should be noted that the relative intensities

*It is interesting to note the presence upon deformation (P ∥ G_4, P ∥ G_2) of the strict correlation between the magnitudes of the relative change of the separation along the directions of the G_2 axes which make equal angles with P, and the magnitudes of the shifts of the components of the splitting corresponding to groups of centers distributed along these axes G_2.

of the splitting constituents in the E ⊥ P-component (with P ∥ G_4) and the E ∥ P-component (with P ∥ G_2) deviate somewhat from the values calculated for isotropic excitation of the luminescence. The deviation is in the direction of the ratios computed for polarized luminescence with absorbing π-oscillators. Apparently, the wide spectral range of the exciting light caused a partial polarization of the line luminescence.

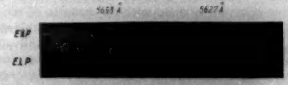


Fig. 5. The splitting of the luminescence lines λ5627 A and λ5698 A of x-rayed LiF upon compression of the crystal along a symmetry axis of second order (L ∥ G_4).

Upon deformation of the crystal, a number of other lines—λ5627 A, λ5830 A, and λ6246 A—also show polarized splitting which is completely similar to the splitting of λ5698 A (see, for example, Fig. 5).* Consequently,

*The long wavelength members of the series also show polarized splitting upon deformation; however, because of the insufficient differentiation of the structure of these rather wide bands a reliable analysis of them is difficult.

these lines, as well as the lines of the equidistant series with its main line at λ5698 A, are connected with anisotropic centers directed along $6G_2$, and correspond to π-oscillators.* Moreover, the closeness in the magnitudes

*Our results agree with recently published data [10] indicating that the line luminescence in LiF is polarized and that the azimuthal dependence of its degree of polarization corresponds to an orientation of the centers along G_2.

of the splitting of different lines can indicate that all emission lines whose relative intensities vary considerably in samples of different history[11] are connected with one type of center (that is to say, oriented in the lattice also along $6G_2$, like the luminescing color centers in LiF, which give the side emission band at λ690 mμ[12]). Also attracting attention is the fact that the splitting of the lines in LiF surpasses by an order of magnitude that observed by us in crystals of $CaF_2:RE^{+++}$ for approximately the same deformation of the crystals. This evidently speaks against the existing theories concerning the connections between the line spectrum of LiF and rare-earth impurities.

The effect of uniaxial compression on the very intense visible absorption line of LiF λ5235 A was also investigated.[10]* It turned out that uniaxial compression of

*Investigation of the action of a magnetic field on λ5235 A disclosed only a displacement to the blue of only ~ 0.02 A for H = 26,700 oersteds.[13]

the crystal along G_4 gave rise to some broadening of the

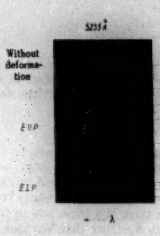


Fig. 6. The splitting of the absorption line λ5235 A of x-irradiated LiF upon compression of the crystal along a symmetry axis of second order ($L \parallel G_2$).

line, along with a significant (~7 cm^{-1} for p = 15 kg/mm^2) displacement toward the blue. Investigation in polarized light showed that the center of the line observed in the E ∥ P-component does not fall directly on the center of the line observed in the E ⊥ P-component. Thus, the broadening of the line seems to be due to an unresolved complex composed of at least two polarized components. Compression of the crystal along G_2 produces another splitting of λ5235 A (Fig. 6). In addition, in the E ∥ P-component two components are observed whose separation equals approximately 11 cm^{-1} for p = 15 kg/mm^2. Close to the long wavelength component is a single broad line, observable in the E ∥ P-component. The incomplete resolution of the splitting structure of λ5235 A in uniaxial compression of the crystal makes analysis of the pattern difficult. Therefore, the question of the orientation of the centers of line absorption in the lattice of LiF requires further investigation.

It should be noted that all of these displacement and splitting phenomena are completely reversible. The magnitudes of the displacements and splittings are proportional to pressure; upon removal of the stress the spectra return to the usual appearance characteristic of the free crystals. This indicates a direct connection between these phenomena and the reversible elastic displacements in the lattice brought about by compressing the crystals.

Thus, the present investigation of the effect of uniaxial compression of a series of crystals on their spectra has, in a number of cases, permitted the determination of the orientation of the local anisotropic centers in the lattice and the nature of the elementary oscillators of the lines in the spectra of the centers (see table). These examples also illustrate the possibility of utilizing the proposed method of investigation along with other existing

Line λ (A)	Orientation of the centers	Type of oscillators	Line λ (A)	Orientation of the centers	Type of oscillators
CaF_2 - Eu	$4\,G_2$		LiF	$6\,G_2$	
5795		π_z	5698		π_z
5808		σ_{xy}	5627		π_z
5282		π_z			
CaF_2 - Sm	$4\,G_3$		5830		π_z
5710		π_z	6246		π_z
5720		σ_{xy}			

methods[9, 15] for the study of local anisotropic centers in cubic crystals.

In conclusion, the author expresses many thanks to E. F. Gross for his interest in the work.

REFERENCES

1. A. A. Kaplyanskii. Opt. i Spektr. 7, 677 (1959).
2. Ya. Ya. Kirs. Trudy Inst. Fiz. i Astron. Akad. Nauk Eston SSR 4, 108 (1956).
3. W. Maisch and H. Drickamer. J. Phys. Chem. Solids 5, 328 (1958);
R. Parsons and H. Drickamer. J. Chem. Phys. 29, 930 (1957);
T. Slykhouse and H. Drickamer. J. Chem. Phys. 27, 1226 (1957); J. Phys Chem. Solids 7, 207, 275 (1958).
4. E. F. Gross, B. S. Razbirin, and M. A. Yakobson. Zhur. Tekh. Fiz. 27, 207 (1957);
E. F. Gross and B. S. Razbirin. Zhur. Tekh. Fiz. 27, 2173 (1957); Zhur. Tekh. Fiz. 28, 237 (1958);
E. F Gross and V. V. Sobolev. Zhur. Tekh. Fiz. 26, 1622 (1956).
5. V. L. Broude, O. S. Pakhomova, A. F. Prikhot'ko, V. V. Eremenko, and V. S. Medvedev. Opt. i Spektr. 2, 323 (1957); Ukrain Fiz. Zhur. 3, 237 (1958).
6. I. V. Stepanov and P. P. Feofilov, Doklady Akad. Nauk SSSR 108, 615 (1956).
7. P. P. Feofilov. Doklady Akad. Nauk SSSR 99, 731, 975 (1954).
8. V. A. Arkhangel'skaya and P. P. Feofilov. Opt. i Spektr. 4, 602 (1958).
9. M. A. El'yashevich. "Spektry redkikh zemel'." (Spectra of the Rare Earths) GITTL, Moscow, 1953.
10. P. Pringsheim and C. Delbecq. J. Chem. Phys. 21, 794 (1953); Z. Physik 136, 573 (1954).
11. A. A. Kaplyanskii. Opt. i Spektr. 6, 424 (1959).
12. P. P. Feofilov. Doklady Akad. Nauk SSSR 93, 743 (1953).
13. G. Joos and H. Ritz. Verhandl. dent. physik. Ges. 7, 101, (1956).
14. A. A. Kaplyanskii, Materialy VII Soveshch. po liuminestsentsii, Moscow, 1958. (Proceedings of the 7th Conference on Luminescence, Moscow, 1958).
15. P. P. Feofilov, Uspekhi Fiz. Nauk 58, 69 (1956).
16. P. P. Feofilov. Opt. i Spektr. 6, 426 (1959).

ON THE INFLUENCE OF INFRARED LIGHT ON LUMINESCENCE OF ZnS-Mn PHOSPHORS

P. B. Jaszczyn

Received 5 March 1959

The effects of infrared light on the blue and orange bands of ZnS-Mn were studied at various constant levels of excitation intensity for different Mn contents and different temperatures. A possible mechanism of sensitization of orange light is presented.

The luminescence of phosphors at low temperatures is strongly affected by infrared rays. Flashes induced by infrared light are intensified a hundredfold on going from room temperature to liquid nitrogen temperature. Investigation of the kinetics of the flashes show that the difference is not only confined to intensity. Figure 1 shows the effects of infrared rays on an excited ZnS-Mn(10^{-4})*

*The batch of phosphors for the test was prepared by M. V. Danilova under the supervision of A. A. Cherepnev. I wish to express my sincere gratitude to both.

phosphor at room temperature. We see from the graph that at first a small flash appears, but after a short period of time the intensity of luminescence decreases to its original value (without added infrared).

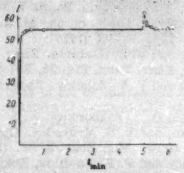


Fig. 1. Effects of infrared light on the intensity of luminescence of a ZnS-Mn(10^{-4}) phosphor at 20°C. Variation of intensity I with time t. Ultraviolet radiation only (solid line); with added infrared light (turned on at t = 5 min) (broken line).

At liquid nitrogen temperature, the phenomenon takes a different course. Figure 2 represents the behavior of the orange and blue luminescence bands which were isolated in this case by use of filters. It is evident that the steady-state intensity of the orange band, which appears in the presence of added infrared, ($_{o}I_{\infty}^{UV+IR}$), is greater than the level achieved without added infrared, ($_{o}I_{\infty}^{UV}$), i.e.,

$$w_o = {}_{o}I_{\infty}^{UV+IR} / {}_{o}I_{\infty}^{UV} > 1.$$

At the same time the steady-state intensity of the blue band is reduced by the added infrared, i.e.,

$$w_T = {}_{T}I_{\infty}^{UV+IR} / {}_{T}I_{\infty}^{UV} < 1.$$

This variation of the spectrum of the steady-state luminescence of ZnS-Mn(10^{-4}) under the influence of infrared rays was the subject of further experiments. It was shown that:

1. The weaker the exciting ultraviolet light, the greater the change in the luminescence spectrum of ZnS-Mn(10^{-4}) produced by infrared illumination, i.e., as the intensity of the exciting light decreases, the quantities $|1 - w_o|$ and $|1 - w_T|$ increase.

2. An increase in the concentration of the activator (manganese) from 10^{-4} gm/gm of ZnS to 10^{-3} gm/gm of ZnS decreases the quantity $|1 - w_o|$.

3. If an additional activator (e.g., cobalt) is introduced into the phosphor then added infrared light quenches the blue band more strongly than the orange one. At the same time the increase in the intensity of the orange band is smaller than without cobalt.

These behavior patterns, and the observed quenching effects of infrared illumination on the blue luminescence on nonactivated ZnS taken from the same batch of phosphors, led to the conclusion that infrared light not only releases electrons from the trapping levels (this is substantiated by the appearance of a flash in the blue band) but also releases holes from the ionized blue centers. Some free holes are relocated on the blue centers, and some recombine with trapped electrons without radiation, which leads to the quenching. In the presence of an activator (manganese for the holes released from the blue centers) there appears an additional possibility of localization on the nonexcited centers of orange luminescence. The latter process signifies the transition of the excitation from a blue to orange band.

For a more detailed study of the effects of infrared illumination, the phosphor luminescence spectra were investigated with and without infrared illumination. Monochromatic infrared radiation was used for this purpose. Figure 3 shows the luminescence spectra of nonactivated ZnS without illumination, and with illumination at approximately equal energy levels, but at different wavelengths λ_{IR} ranging from 695 mμ to 1884 mμ. As can be seen, the added infrared caused the quenching and broadening of the blue luminescence band of ZnS. In the range investigated, the quenching effect of infrared increased with increasing λ_{IR}. We shall return to the question of the broadening of the blue band under the influence of infrared light.

Figure 4 shows ZnS-Mn(10^{-4}) spectra photographed under similar conditions. Comparison of Figs. 3 and 4 shows that the addition of manganese increases the quenching effects of infrared illumination on the blue band. This should be expected, since the addition of manganese decreases the probability of relocation of free holes on blue centers by the introduction of new luminescence centers and local energy levels.

Considering the spectral changes in the luminescence to be solely the result of the release of the holes from the blue centers and their partial localization on orange centers, one might expect that the ratio of ΔN_o, the number of additional quanta of orange luminescence (produced by the illumination), to ΔN_T, the number of quanta of blue luminescence quenched by added infrared, will be constant, and obviously less than one. In the diagrams shown the areas of the corresponding regions of the spectra between the luminescence curves with and without infrared illumination are proportional to ΔN_o and ΔN_T. It is seen from Fig. 4 that the ratio of these quantities is a function of wavelength λ_{IR}. It is large for $\lambda_{IR} < 1\mu$. For the shortest λ_{IR} investigated, it considerably exceeds unity, (for λ_{IR} = 775 mμ, $C = \Delta N_o / \Delta N_T \approx 2$).

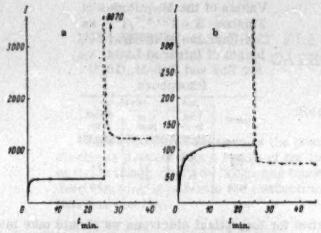


Fig. 2. Effects of infrared light on the intensity of luminescence of a ZnS-Mn(10^{-4}) phosphor at −190°C. a—orange band, b—blue band. Variation of intensity of luminescence I with time t. Ultraviolet radiation only (solid line); with added (at t = 25 min) infrared (broken line).

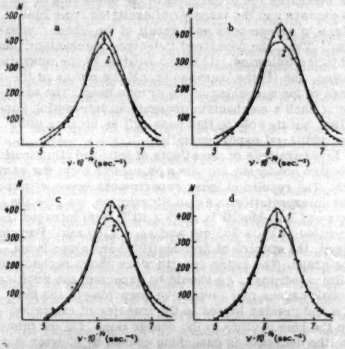


Fig. 3. Effects of infrared light on the luminescence spectrum on nonactivated ZnS phosphor at −190°C. Curve 1—for excitation by a single wavelength of ultraviolet (λ = 366 mμ). Curve 2—with added infrared of various wavelengths; a—695 mμ, b—775 mμ, c—900 mμ, d—1184 mμ.

The last result shows that, in this case, infrared illumination increases the total number of quanta emitted by the phosphor. The latter fact explains the decrease of the quenching.

The quenching, as is known, is due to the radiationless recombination of free holes with the trapped electrons. We have already mentioned the release of the holes by infrared light. However, free holes exist in the phosphor even in the absence of infrared illumination. They are generated by the exciting light itself. Since infrared light also ejects electrons from local levels it thereby decreases the number of radiationless recombinations of free holes, and thus decreases the quenching of luminescence. The infrared quenching effect observed in ZnS is a result of the superposition of two processes: the release of holes, which decreases the luminescence, and the release of electrons, which increases the luminescence. Thus, without additional experiments, it is impossible from Fig. 3 to draw any conclusion as to which wavelength of infrared is most effective in releasing holes from the blue luminescence centers.

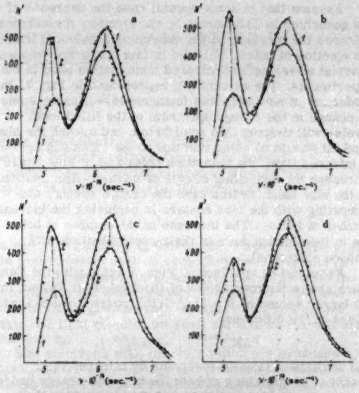


Fig. 4. Effects of infrared light on the luminescence spectrum of a ZnS-Mn(10^{-4}) phosphor at −190°C. Curve 1—for excitation by a single wavelength of ultraviolet (λ = 366 mμ). Curve 2—with added infrared light of various wavelengths; a—695 mμ, b—775 mμ, c—900 mμ, d—1184 mμ.

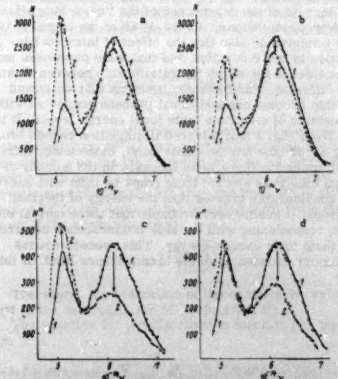


Fig. 5. Comparison of effects of the influence of infrared illumination on the luminescence spectrum of ZnS-Mn(10^{-4}) phosphors, (a and b) ZnS-Mn(10^{-4}), Co(5.10^{-4}), (a and b). Curve 1—Excitation by only one wavelength (λ = 366 mμ). Curve 2—with added infrared light of various wavelengths; a and d—755 mμ, b and c—1280 mμ.

Assume that in some special case the decrease of the quenching in ZnS caused by the ejection of electrons balances the increase of the quenching associated with the ejection of holes. This did in fact occur for the shortest wavelength of infrared illumination used in the experiments. The results are represented in Fig. 3. Introduction of new additives (manganese)—if one assumes no change in the energy spectrum of the filled local levels—will destroy this equilibrium and quench the blue band. It should be noted that due to the "flashing action" of infrared light, the transition from ZnS to ZnS-Mn(10^{-4}) increases the quenching effects of infrared illumination on the blue band. In this case the orange spectra are competing with the blue centers in capturing the increased number of holes. (The increase in the number of holes is due to the slowing down of their recombination with trapped electrons).

From the comparison of Figs. 3 and 4 with the Table, which shows the magnitudes of the flashes, it follows that the larger values of $R = I^{UV+IR}_{max}/I^{UV}_{\infty}$ correspond to larger values of the difference

$$|\Delta N_T^{ZnS-Mn}| - |\Delta N_T^{ZnS}|.$$

The ejection of trapped electrons by infrared light weakens the quenching of both the blue and orange bands, and thus leads to the increase of $C = |\Delta N_0|/|\Delta N_T|$, since in this case ΔN_0 is increasing and ΔN_T is decreasing. Further comparison of the Table with Figs. 3 and 4 shows that in reality C does not always increase with R. It is true that for $\lambda_{IR} < 1\mu$, both C and R are greater than for $\lambda_{IR} > 1\mu$. On the other hand, however, the most intense of all the flashes, viz., for $\lambda_{IR} = 900$ mμ, corresponds to C values considerably smaller than those obtained for $\lambda_{IR} = 775$ mμ. One should, apparently, take account of the dependence of the "quenching effects" of the trapped electrons on the depth of the traps. It is quite conceivable also that the effect of infrared illumination is more complex, and that some processes must be considered for which the relationship between C and R is different. For instance, it seems that we should take into account one additional process connected with the ejection of electrons from local energy levels. It is seen from Fig. 3 that infrared illumination causes broadening of the blue luminescence band. Since under infrared illumination there is an increase in the number of optical electrons ejected from traps by light with energies considerably greater than the energy of thermal electrons, it seems very probable that these optical electrons, recombining with the blue luminescence centers, give them their excess energy. This process causes oscillatory broadening of the luminescence band. If this is so, then for the optical electrons we should take into account the increased probability of reversion from the blue center excitation level to the conduction zone. Such a process would increase the number of recombinations of ionized orange centers, as if creating for them an increased concentration of free electrons. By thus decreasing the quenching of the orange luminescence, the "electron mechanism" proposed here would increase the life span of a hole localized on the blue center. This process increases the probability of the quenching of the blue centers and the transfer of excitaton from blue centers to orange ones as a result of the "hole mechanism." Thus, the described "electron mechanism" may lead to the following: (1) intensification of the migration of holes, and (2) the increase of ΔN_0 by means of the decrease of the quenching of the orange band. The existence of such a mechanism presents an interesting possibility, but its role in this case will be clearer after some additional experimentation.

Values of the Magnitudes of Flashes, $R = I^{UV+IR}/I^{UV}$, as a Function of the Wavelength of Infrared Light, λ_{IR}, for ZnS and ZnS-Mn(10^{-4}) Phosphors

λ_{IR} mμ	ZnS	ZnS-Mn (10^{-4})	
	blue luminescence	blue luminescence	orange luminescence
695	4.0	3.8	—
775	3.5	3.1	8.4
900	3.7	4.2	10.4
1184	1.7	2.2	5.6

Investigations of the effects of infrared illumination were also conducted for other phosphors from the same batch. The results of these experiments agree with the above interpretations. As an illustration, we give the spectra of ZnS-Mn(10^{-4}), Co(5×10^{-8}) with infrared illumination at $\lambda_{IR} = 755$ mμ and $\lambda_{IR} = 1280$ mμ. For comparison, the spectra of ZnS-Mn(10^{-4}) are given in the same graph. The latter spectra were photographed under similar conditions. As should be expected, the addition of cobalt causes more intensive quenching of the blue bands and greater losses in the transfer of excitation from the blue centers to the orange ones. On the other hand, the decrease in quenching caused by shorter wavelength infrared illumination appears to be more effective in this case than in phosphors without cobalt.

I express my deep gratitude to V. V. Antonov-Romanovskii, Z. N. Trapeznikova, and M. V. Fok for invaluable discussions.

INFLUENCE OF FAST ELECTRONS ON THE LIGHT SUM STORED IN CATHODOLUMINESCENCE

Iu. M. Popov

Received 5 March 1959

An examination is made of the possibility of ejecting electrons from trapping levels by fast electrons produced as a result of the ionization losses of a primary cathode beam. The density of the primary electron beam was found at which the probability of ejecting electrons from fairly deep trapping levels into the conduction band by ionization is comparable with the probability of thermal ejection.

It is known[1] that almost all cathodoluminophors increase their rate of decay of phosphorescence with increasing density of the exciting cathode beam. Some luminophors are an exception (for example, Zn_2SiO_4)[2] and even then within a rather restricted range of excitation density. This increase of the rate of decay with increasing excitation intensity also occurs in photoluminescence, where the phenomenon is explained by the relatively greater occupancy of shallow levels compared with deeper ones as the excitation density increases,[3] and by the activation effect of the exciting light[4] (at high excitation densities). As a rule, cathodoluminescence is associated with greater excitation densities than photoluminescence. Cathodoluminescence should also show relatively greater occupation of the shallow levels as the excitation density increases.

In this paper we want to point out another aspect of the possibility of a decrease in the storage of energy in the deep levels in cathodoluminescence; namely, the ejection of electrons from the trapping levels by fast electrons produced in the conduction band. Since the problem of total energy exchange of the primary electrons of a cathode beam appears to be highly complicated because of the many stages involved in the exchange of energy in a solid (through secondary electrons, tertiary electrons, etc.) and since this problem is still far from solution, we shall not consider it. We assume that although all the electrons in a solid (primary, secondary, and so on) have sufficient energy to elevate an electron from the valence band to the conduction band, the fundamental processes are the ionization processes. Such an assumption is justified, since in the energy range of interest (up to 100 kev) the fundamental energy losses for electrons passing through a solid are associated with ionization.[5] We will therefore assume that the primary electron beam instantaneously* produces electrons in the conduction band of a cristallophosphor, these electrons having a quantity of kinetic energy which is smaller than the width of the forbidden energy gap.

*The time required for ionization losses to occur is smaller than any of the other characteristic times considered.

For our problem, a knowledge of energy distribution of these electrons is important. However, the energy distribution may be obtained only after solving the problem of the total exchange of energy of the primary electrons, the secondary electrons, and so on. Nevertheless, to obtain the effect in question within an accuracy of an order of magnitude, we assume that the distribution of electrons obtained instantaneously as a result of total ionization is of the form $q\delta(\varepsilon - \varepsilon_0)$, where ε_0 is the mean kinetic energy of the conduction electrons and ε is the kinetic energy of an individual electron ($\varepsilon = p/2m$, p is the momentum of an electron, and m is the effective mass of an electron). The problem of what value to assign to the quantity ε_0 has no clear answer. The available experimental data on secondary emission[6] and on the direct penetration of an electron beam[7] indicate the production in the solid of electrons with energies hundreds of times greater than thermal energy. Until we obtain our final results, we shall not consider a definite value for ε_0.

The electrons with energy ε which are produced by ionization lose their energy and reach an equilibrium with the lattice of the cristallophosphor ($\varepsilon_0 > kT$). Slowing down, the electrons recombine both with and without radiation and occupy trapping levels. Conduction electrons with energy greater than the depth of the trapping levels may eject electrons from these levels into the conduction band. This would lead to a smaller storage of energy in these trapping levels than would follow from thermodynamical equilibrium considerations. It is necessary to determine the conditions under which the probability of thermal ejection from the kth trapping level is comparable with the probability of ejection because of ionization by fast electrons, which is $W_i^{(k)}$. It is evident that

$$W_i^{(k)} = \int_{I^{(k)}}^{\infty} \sqrt{\frac{2\varepsilon}{m}}\, \sigma_i^{(k)}(\varepsilon)\, f(\varepsilon)\, d\Gamma. \qquad (1)$$

Here, $f(\varepsilon)$ is the distribution function of the conduction electrons; $\sigma_i^{(k)}(\varepsilon)$ is the ionization cross section of an electron on the kth trapping level by a conduction electron with energy ε; $I^{(k)}$ is the ionization potential of an electron occupying the kth trapping level ($I^{(k)} = \Delta E^{(k)}$, where $\Delta E^{(k)}$ is the depth of the trapping level from the bottom of the conduction band); and

$$d\Gamma(\varepsilon) = \frac{4\sqrt{2}\pi m^{3/2}\sqrt{\varepsilon}\, d\varepsilon}{(2\pi\hbar)^3}.$$

Therefore, the evaluation of the quantity W_i reduces itself to the determination of the function $f(\varepsilon)$.

The equation for the distribution function has the form

$$(a - b)f + q\delta(\varepsilon - \varepsilon_0) + \sum_k \nu_k \int_{I^{(k)}}^{\infty} \omega_{(k)}^{i}(\varepsilon\varepsilon')\, f(\varepsilon')\, d\Gamma(\varepsilon') - f(\varepsilon) = 0. \qquad (2)$$

Here $(a - b)f$ is the collision integral; $\omega_k^{(i)}(\varepsilon\varepsilon')$ is the probability of producing an electron with energy ε by ionization of the kth trapping level by an electron with energy ε'; ν_k is the number of electrons in the kth trapping level; and

$$f(\varepsilon) = \sum_k w_k(\varepsilon) f(\varepsilon) \left(\nu_k^{(0)} - \nu_k\right) - \sum_k P_k(\varepsilon)\nu_k + u(\varepsilon),$$

where $\omega_k(\varepsilon)$ is the probability of occupancy of the kth traping level by an electron with energy ε. P_k is the probability of thermal ejection from the kth trapping

level into the level ε; $\nu_k^{(0)}$ is the number of trapping levels of the kth type, and the quantity $u(\varepsilon)$ characterizes the transfer of electrons with energy ε into the valency band directly, and through all the possible capture levels with the exclusion of the trapping levels. We leave out the processes of tertiary recombination, since such recombination requires high excitation densities[8] which we will not consider here.

The distribution function for energy $\varepsilon > I^{(k)}$ enters into Eq. (1). It will be shown below that the effect in question is observed for $I^{(k)} \gg kT$, and therefore we shall solve Eq. (2) for the range $\varepsilon \gg kT$. However, for $\varepsilon \gg kT$, the last two terms in Eq. (2) may be considered as a perturbation with respect to the first two principal terms. This is due to the fact that only the slowest electrons recombine ($\omega_k(s)$, $P_k(\varepsilon)$, and $u(\varepsilon)$ decrease rapidly when $\varepsilon > kT$). The third term of Eq. (2) is usually small, since $\omega_n^{(k)}(\varepsilon\varepsilon')\nu_k$ is smaller than the probability of scatter due to lattice vibration ($\nu_k \ll N$, where N is the number of atoms of the substance in 1 cm^3).

To determine the form of the distribution function for $\varepsilon \gg kT$ we solve the equation

$$(a-b)f + q^0(\varepsilon - \varepsilon_0) = 0. \tag{3}$$

The normalizing factor of the distribution function is determined from the condition imposed on $j(\varepsilon)$. Equation (3) may be written in the following form

$$\frac{1}{\sqrt{2m\varepsilon}}\frac{dS_\varepsilon}{d\varepsilon} = q^0(\varepsilon - \varepsilon_0)\Big|_0, \tag{4}$$

where S_ε is the electron current in energy space. The specific form of S_ε depends on the type of lattice vibration of the crystal. Since the majority of cathodoluminophors possess ionic bonds to some degree and since within the energy range of interest the cross-section for scattering due to vibration of the ionic lattice is greater than the cross-section for scattering due to acoustic and other types of vibration, we shall only consider the scattering due to optical vibrations of the ionic lattice. For simplicity, we shall consider a cubic diatomic lattice. We shall take $kT \gg \hbar\omega_0$, where ω_0 is the Debye frequency. From the work of Davydov and Shmushkevich[9] we have

$$S_\varepsilon = -\frac{2\pi m\gamma^2 Z^2 e^4}{M a^3}\ln\frac{4\varepsilon}{\hbar\omega_0}\left[f + kT\frac{df}{d\varepsilon}\right], \tag{5}$$

where

$$M = \frac{M_+ M_-}{M_+ + M_-},$$

$M_\pm$ being the masses of the positive and negative ions, respectively. Ze is the charge on each ion and a is the interionic distance.

The difference of γ from unity is determined by the deformation of the electronic shells due to the vibration of the ions. For not too strongly heteropolar compounds, γ may very likely be considerably smaller than 1.

Multiplying Eq. (4) by $d\Gamma$ and integrating from ∞ ($S = 0$ for $\varepsilon \to \infty$) to ε, we obtain

$$f + kT\frac{df}{d\varepsilon} = 0; \quad \varepsilon > \varepsilon_0 \tag{6}$$

and

$$\ln\frac{4\varepsilon}{\hbar\omega_0}\left[f(\varepsilon) + kT\frac{df}{d\varepsilon}\right] = R; \quad \varepsilon < \varepsilon_0, \tag{7}$$

where

$$R = \frac{Q\tau_\varepsilon kT(2\pi\hbar)^3}{(\hbar\omega_0)^3\sqrt{2mkT}\cdot 2\pi m}; \quad \frac{1}{\tau_\varepsilon} = \frac{\pi\gamma^2 Z^2 e^4\sqrt{2mkT}}{Ma^3(\hbar\omega_0)^3}. \tag{8}$$

Here Q is the number of electrons (in cm^{-3} sec^{-1}) with energy ε_0 which are produced by multiplication of the primary electron beam. We have

$$Q = \int_0^\infty q^0(\varepsilon - \varepsilon_0)\,d\Gamma. \tag{9}$$

The distribution function for $\varepsilon > \varepsilon_0$ has the form

$$f(\varepsilon) = C_2 e^{-\frac{\varepsilon}{kT}}. \tag{10}$$

In the range $kT \ll \varepsilon < \varepsilon_0$ we have

$$f(\varepsilon) = e^{\frac{\varepsilon}{kT}}\left(R\int_{\frac{\varepsilon_0}{kT}}^{\frac{\varepsilon}{kT}}\frac{e^t dt}{\ln \alpha t} + C_2\right), \tag{11}$$

where

$$\alpha = \frac{4kT}{\hbar\omega_0}.$$

From the boundary conditions for solutions of (10) and (11) at $\varepsilon = \varepsilon_0$ we have

$$C_1 = C_2$$

The constant C_2 should be determined from the fact that the current of electrons ejected into the conduction band equals the current due to electrons leaving the conduction band because of recombination. The latter may be obtained by multiplying Eq. (2) by $d\Gamma$ and integrating it over all energies

$$\int_0^\infty j(\varepsilon)\,d\Gamma = Q. \tag{12}$$

As was shown earlier, all of the recombination is essentially due to electrons with energy $\varepsilon \ll kT$. Therefore, in the left-hand side of Eq. (12) the limits of integration are, in fact, from 0 to kT. However, it is just within this range that Eq. (7), from which the function $f(\varepsilon)$ is derived, is not correct. Therefore, we shall write (12) as a boundary condition for current at the boundary $\varepsilon = kT$, that is,

$$j(kT)\int_0^{kT} d\Gamma = Q, \tag{13}$$

considering that for $\varepsilon = kT$ there is a flow of recombining electrons. An analogous argument is used when studying the problem of dielectric and semiconductor breakdown.[10] Introducing $\tau_{n\tau}$, the lifetime with respect to recombination, we obtain

$$j(kT) = f(kT)\frac{1}{\tau_{n\tau}}. \tag{14}$$

Determining the constant C_2 from Eq. (14), we obtain the following distribution function for $kT \ll \varepsilon < \varepsilon_0$

$$f(\varepsilon) = \frac{9}{4}\left(\frac{\hbar\omega_0}{kT}\right)^2\frac{\tau_{n\tau}}{\tau_\varepsilon}\cdot Re^{-\frac{\varepsilon}{kT}} + Re^{-\frac{\varepsilon}{kT}}\int_1^{\frac{\varepsilon}{kT}}\frac{e^t dt}{\ln(\alpha t)}. \tag{15}$$

The first term of distribution function (15) is the usual Maxwellian distribution of electrons which collide with the lattice; the second term reflects the presence of high energy electrons due to the continuous source $q^0(\varepsilon - \varepsilon_0)$. Since $\hbar\omega_0 < kT$ (as a rough approximation, we take $\hbar\omega_0 \approx kT$) and for the constants which characterize the substance ZnS (we assume $Z = 1$, $\gamma = 1$, $M = 38640m$, $a = 3 \times 10^{-8}$cm), we have $\tau_\varepsilon \approx 10^{-13}$sec, so that $\tau_{n\tau} \gg \tau_\varepsilon$.

Therefore the second term in $f(\varepsilon)$ begins to be of importance only when the energy

$$\varepsilon \geqslant kT \ln\left(\frac{\tau_{nr}}{\tau_r}\right).$$

It follows from this that in evaluating $W_t^{(k)}$ according to formula (1) for the trapped electrons with ionization potential

$$I^{(k)} \geqslant kT \ln\left(\frac{\tau_{nr}}{\tau_r}\right)$$

we take only that part of function (15) which corresponds to the non-Maxwellian distribution. It is, in fact, this part of $f(\varepsilon)$ which describes the activating effect of fast electrons on the trapping levels, differentiates cathodoluminescence from photoluminescence. It should be noted that the lifetime τ_{nr} does not enter at all into this part of $f(\varepsilon)$ and that the effect which we look for is therefore independent of the process of recombination. For $W_t^{(k)}$ we have

$$W_t^{(k)} = R \int_{I^{(k)}}^{\infty} d\tau \left[\sqrt{\frac{2\varepsilon}{m}}\, \sigma_i^{(k)}(\varepsilon) e^{-\frac{\varepsilon}{kT}} \int_1^{\frac{\varepsilon}{kT}} \frac{e^t dt}{\ln(\alpha t)} \right]. \qquad (17)$$

In place of the upper limit, which is equal ∞ in Eq. (1) we take ε_0, since according to Eq. (10), the distribution function decreases rapidly for $\varepsilon > \varepsilon_0$.

The behavior of the ionization cross section for the deep levels of impurities is unknown. To make an estimate, we shall make the approximation that this cross section is similar to that of hydrogen, with a maximum at $\varepsilon = 3I^{(k)}$. We shall take into account the enlargement of the orbit due to the dielectric constant of the substance (dielectric constant $D \approx \sqrt{E_R/I^{(k)}}$)

$$\sigma_i^{(k)}(\varepsilon) = \sigma_0 \frac{E_R}{\varepsilon} \ln \frac{\varepsilon}{I^{(k)}}, \qquad (18)$$

where σ_0 is the ionization cross section of hydrogen at the maximum and E_R is the Rydberg energy.

The integrals in Eq. (17) are not included in the elementary functions. Therefore, to make an estimate we take out $1/\ln(\alpha\tau)$ as a slowly varying function, taking $\ln(\alpha\tau) = \ln(\alpha(\varepsilon_0/kT))$, since the region $\varepsilon \approx \varepsilon_0$ makes the greatest contribution in Eq. (17). Assuming $\ln\varepsilon_0/I^{(k)} > 1$, we obtain from Eqs. (17) and (18)

$$W_t^{(k)} = \frac{\sigma_0 M a^2 E_R^2 q Q \ln\left(\frac{\varepsilon_0}{I^{(k)}}\right)}{\pi m \gamma^2 Z^2 e^4 \ln\left(\frac{\alpha\varepsilon_0}{kT}\right)}. \qquad (19)$$

We shall compare the value obtained for the probability of ionization from the kth trapping level by fast electrons with the probability of thermal ejection from this level, which is equal to

$$\int_0^{\infty} P_k(\varepsilon)\, d\Gamma(\varepsilon) = W_{nr}^{(k)} \left(\frac{2(2\pi mkT)^{3/2}}{(2\pi\hbar)^3} \right) e^{-\frac{\Delta H^{(k)}}{kT}}. \qquad (20)$$

Here $W_{nr}^{(k)}$ is the probability of radiationless electron occupancy of the kth level. To compare Eq. (19) with Eq. (20) it is still necessary to choose a value for ε_0. Experiments on secondary emission[2] and on direct penetration of matter by an electron beam[7] indicate that the main products in the solid are electrons with energies of from 1 to 10 ev. For an estimate we shall take $\varepsilon_0 = 3$ ev, which corresponds to the width of the forbidden energy band in the usual cathodoluminophors (ZnS). Assuming the cross section for the radiationless occupancy of a trapping level by an electron to be $\sigma_{nr} \approx 10^{-16}\,\text{cm}^2$ and also that most of the electrons captured have velocities below the thermal value, and taking all the constants for the substance ZnS at 300°K, we obtain

$$W_t^{(k)} > \int_0^{\infty} P_k d\Gamma$$

for

$$Q > 10^{23} e^{-\frac{I^{(k)}}{kT}}. \qquad (21)$$

It follows from (21) that with increasing of the cathode beam density, the effect under consideration will appear first in the deepest trapping levels. Therefore for such deep levels as $I^{(k)} = 10\ kT$ ($I^{(k)} = 0.3$ ev at T = 300°K) the phenomenon of ejection by fast electrons begins at $Q \approx 10^{23}$ particles/cm² sec. Such excitation densities are easily attainable. For an incident beam of density i amp cm^{-2}, and with an accelerating voltage V (we shall take V = 30 kev) we have

$$Q \approx \frac{iV}{M}, \qquad (22)$$

where δ is the energy expended to produce one fast electron in the conduction band ($\delta \approx 6$ ev), and l is the depth of electron penetration (for V = 30 kev, according to reference 11, $l \approx 10^{-4}$ cm). Consequently, for the parameters chosen, $Q \approx 10^{23}$ for $i \approx 10^{-4}$ amp cm^{-2}.

The estimate obtained for i should be decreased for ordinary cathodoluminophors (e.g., ZnS). In making the estimate, we assumed $\gamma^2 = 1$, i.e., we took a strongly heteropolar crystal. It is known that the most common cathodoluminophors do not appear to be very strongly heteropolar compounds. In our case ($\gamma^2 = 1$) the free path of a conduction electron of energy $\varepsilon \approx 10kT$ is $l = 10^{-7}$ cm, while the available experimental material[12] gives for the optical electrons ($\varepsilon > kT$) $l \approx 10^{-6}$ cm. We therefore consider that in our case (ZnS) the quantity $\gamma^2 = 0.1$ and, consequently, that for the above chosen parameters of excitation, the ionization of trapped electrons will occur at $i = 10^{-3}$ amp cm^{-2}.

This effect imposes a limit on the magnitude of the light sum stored in the deep levels, depending on the excitation density. According to Eq. (19), ionization from the trapping level $W_t^{(k)}$ is, in fact, independent of temperature, and the probability of thermal ejection decreases exponentially as the temperature becomes lower. Therefore as the temperature decreases, the ionization probability becomes comparable with the probability of thermal ejection for considerably lower densities (according to Eq. (19), for instance, for a decrease of temperature from T = 300°K to T = 150°K, the ionization probability does not change, but the probability of thermal ejection decreases by an order of magnitude). If at any given temperature and excitation density the ionization probability from a certain trapping level is comparable with the probability of thermal ejection then, under such conditions there is no increase in the light sum stored in this level if the temperature decreases or the excitation density increases.

In conclusion, the author expresses his gratitude to V. A. Chuenkov for several valuable comments.

REFERENCES

1. A. V. Moskvin. "Katodoliuminestsentsiya" ch. I. (Cathodoluminescence, Part I), Gostekhizdat, 1948.
2. P. A. Einstein. Brit. J. Appl. Phys. 8, 190 (1957).

3. Iu. M. Popov. Opt. i spektr. 6, 764 (1959).
4. V. V. Antonov-Romanovskii. Izv. Akad. Nauk SSSR, Ser. Fiz. 15, 637 (1951).
5. L. D. Landau and E. M. Lifshits. "Elektrodinamika sploshnykh sred." (Electrodynamics of Continuous Media), Gostekhizdat, 1957.
6. N. R. Whetten and A. B. Laponsky. Phys. Rev. 107, 1521 (1957).
7. N. B. Gornyi. Zhur. Eksp. i Teoret. Fiz. 35, 281 (1958); Soviet Phys.—JETP 8, 193 (1959).
8. Iu. M. Popov and V. P. Shabanskii. Opt. i spektr. 6, 769 (1959).
9. B. Davydov and I. Shmuchkevich. Zhur. Eksp. i Teoret. Fiz. 10, 1043 (1940).
10. V. A. Chuenkov. Izv. Akad. Nauk SSSR, Ser. Fiz. 33, 389 (1958).
11. W. Ehrenberg and J. Franks. Proc. Phys. Soc. B66, 1057 (1953).
12. E. S. Rzhanova. Trudy Fiz. Inst. Akad. Nauk 7, 47 (1956).

SPECTRAL CHARACTERISTICS OF ELECTROLUMINESCENCE OF SOME ELECTROLUMINOPHORS IN THE CASE OF THE SIMULTANEOUS ACTION OF CONSTANT AND ALTERNATING FIELDS

V. N. Favorin, G. S. Kozina, and L. K. Tikhonova

Received 10 March 1959

An electroluminescent layer made from a luminophor containing manganese as the activator is capable of producing light when a constant potential difference is applied to it. A bright electroluminescence in a constant electric field is found in so-called two-color electroluminophors (of the type ZnS-Cu, Mn, which have green and yellow bands in an alternating field) as well as in mechanical mixtures of single-color luminophors which contain a yellow electroluminophor activated by manganese.

Two-color electroluminophors with specially chosen activator ratios, as well as mixtures of single color electroluminophors of a corresponding composition, have different luminescent spectral characteristics in constant and alternating fields.

An investigation of the spectral distribution was conducted with a UM-2 monochromator and a FEU-27 photoelectric multiplier of known spectral sensitivity. The electroluminescent layer was fabricated from luminophors in a dielectric medium (in mixtures of melamine-formaldehyde and bakelite-type resin or in silicone lacquers). A transparent conducting film of tin oxide on glass and a vacuum evaporated layer of aluminum served as electrodes. Both dc and ac voltages (frequency 500 cps) were applied across the electrodes; their magnitudes and the magnitude of the direct current were controlled by instruments included in the circuit. The thickness of the samples under investigation was 100 μ.

Figure 1 shows the spectral characteristics of the luminescence from a layer made of a mixture of ZnS-Cu and ZnS-Cu, Mn luminophors in a constant (curve 1) and an alternating (curve 2) field. As can be seen in this figure, the electroluminescence of the layer in a constant field is characterized by a maximum in the yellow, (λ_{max} = 580 mμ), whereas the same layer has a green luminescence (λ_{max} = 510 mμ) in an alternating field.

The spectral characteristics of luminescence in constant and alternating fields for a layer prepared from a two-color luminophor is shown in Fig. 2.

In the case of simultaneous constant and alternating fields, the color of the luminescence varies with the ratio of the field components. Figure 3 shows the spectral characteristics of electroluminescence of a layer in a constant field (curve 1) and under the simultaneous action of this same constant field and alternating voltages of different amplitudes (curves 2, 3, and 4). The dashed curves 2a, 3a, and 4a represent the spectral characteristics of the same layer excited only by alternating voltages of the same amplitudes. It follows from Fig. 3 that as the amplitude of the alternating voltage increases, a maximum in the green first appears and then increases. Thus, changing the amplitude of the alternating field while keeping the dc field constant causes the color of the luminescence of the layer to change from yellow (λ_{max} = 580 mμ) to green (λ_{max} = 510 mμ).

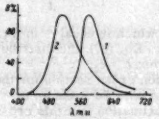


Fig. 1

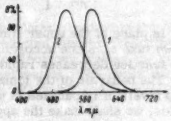


Fig. 2

Fig. 1. The spectral characteristics of the electroluminescence of a layer composed of a mixture of ZnS-Cu and ZnS-Cu, Mn luminophors in a dc (1) and an ac (2) field. Constant voltage $V_{=}$ = 1300 volts; constant current $I_{=}$ = 800 μamp; ac voltage $V_{\sim}$ = 400 volts. Fig. 2. The spectral characteristics of a two-color electroluminophor ZnS-Cu, Mn in a dc (1) and an ac (2) field. $V_{=}$ = 800 volts, $V_{\sim}$ = 500 volts (symbols as under Fig. 1).

A change of color in the luminescence of the layer can also be brought about by increasing the constant voltage while the alternating field is kept constant. The spectral characteristics under these conditions are shown in Fig. 4. Curves 1a, 1b, and 1c represent the spectral characteristics of luminescence of the layer in constant fields of different magnitudes (V = 1050, 1200, and 1400 volts). Curves 2a, 2b, and 2c show the luminescent spectral characteristics of the layer under simultaneous action of each of the indicated constant voltages and a single alternating voltage (the spectral distribution curve for this alternating voltage is shown in Fig. 4, curve 3).

From an analysis of the curves in Figs. 3 and 4, it follows that under the simultaneous action of a constant and an alternating voltage there is observed, first of all, an increase in the luminescent intensity in the yellow part of the spectrum, and secondly, the intensity of this

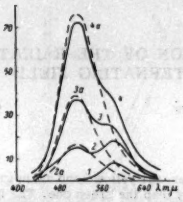


Fig. 3. Spectral characteristics of the electroluminescence of a layer under the action of a dc (1), ac (2a, 3a, and 4a) and the simultaneous action of a dc and an ac field of different amplitudes (2,3,4).
Curve 1—$V_{=}$ = 1100 volts, $V_{\sim}$ = 0, $I_{=}$ = 100 μamp;
curve 2—$V_{=}$ = 1100 volts, $V_{\sim}$ = 220 volts, $I_{=}$ = 100 μamp;
curve 3—$V_{=}$ = 1100 volts, $V_{\sim}$ = 280 volts, $I_{=}$ = 100 μamp;
curve 4—$V_{=}$ = 1100 volts, $V_{\sim}$ = 400 volts, $I_{=}$ = 100 μamp;
curve 2a—$V_{=}$ = 0, $V_{\sim}$ = 220 volts, $I_{=}$ = 0;
curve 3a—$V_{=}$ = 0, $V_{\sim}$ = 280 volts, $I_{=}$ = 0;
curve 4a—$V_{=}$ = 0, $V_{\sim}$ = 400 volts, $I_{=}$ = 0
(symbols as under Fig. 1).

luminescence is greater than the sum of the intensities of the field components acting separately.

In the case shown in Fig. 3, when the constant field acts simultaneously with the alternating field, the brightness of the yellow maximum of the spectral characteristic is greater by a factor of 1.5 to 2 than the brightness for the same constant voltage alone; furthermore, the brightness is between 20 and 30% greater than the sum of the brightnesses of each of the field components acting separately.

In the green part of the spectrum, one observes the opposite kind of effect when the constant field is added in; the luminescent brightness becomes somewhat less than it was under the action of the alternating field alone.

One can surmise that such a change in the spectral characteristics occurs because the constant voltage affects luminophors made with various activators (copper and manganese) in different ways, and, obviously, such a change is the result of different electroluminescence mechanisms active in these luminophors when they are placed in an ac field.[1] The nonadditivity of the effects caused by the constant and alternating fields leads to the assumption that, when the constant and variable voltages act simultaneously, one observes not only the independent electroluminescent phenomena which occur when the fields are acting separately, but also the effect of one of the field components on the electroluminescence associated with the other.

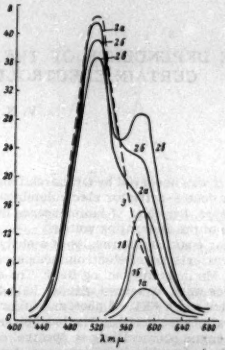


Fig. 4. Spectral characteristics of the electroluminescence of a layer under the action of a dc (1a, 1b, and 1c), an ac (3) and under the simultaneous action of a dc and an ac field of different amplitudes (2a, 2b, and 2c).
Curve 1a—$V_{=}$ = 1050 volts, $V_{\sim}$ = 0, $I_{=}$ = 55 μamp;
curve 1b—$V_{=}$ = 1200 volts, $V_{\sim}$ = 0, $I_{=}$ = 100 μamp;
curve 1c—$V_{=}$ = 1400 volts, $V_{\sim}$ = 0, $I_{=}$ = 200 μamp;
curve 2a—$V_{=}$ = 1050 volts, $V_{\sim}$ = 280 volts, $I_{=}$ = 55 μamp;
curve 2b—$V_{=}$ = 1200 volts, $V_{\sim}$ = 280 volts, $I_{=}$ = 100 μamp;
curve 2c—$V_{=}$ = 1400 volts, $V_{\sim}$ = 280 volts, $I_{=}$ = 200 μamp;
curve 3—$V_{=}$ = 0, $V_{\sim}$ = 280 volts, $I_{=}$ = 0
(symbols as under Fig. 1).

The spectral characteristics presented in this paper show that in the case of simultaneous application of ac and dc voltages to electroluminescent layers composed of two-color electroluminophors containing manganese as one of the activators, or to mixtures of single color electroluminophors which include a yellow manganese-activated luminophor, the color of the luminescence changes as the ratio of the field components is changed.

For the luminophors which were investigated, the largest shift of the maximum in the spectral characteristic amounted to 70 mμ. This limit does not seem to have any theoretical significance, however, and if a different electroluminophor (with a shorter wavelength maximum) is used in place of the green one, the color of the light should change over wider spectral limits.

REFERENCE

1. P. Zalm. Phil. Res. Rep., 11, 353, 417, (1956).

VOLTAGE DEPENDENCE OF THE SPECTRAL COMPOSITION OF THE RADIATION FROM CERTAIN ELECTROLUMINOPHORS IN AN ALTERNATING FIELD

V. N. Favorin and L. P. Poskacheyeva

Received 10 March 1959

In 1957, it was observed by Oranovskii and Trapeznikov that for double-activator electroluminophors of the ZnS-Cu, Mn type, the color of luminescence depends on the amplitude of the alternating voltage.

This paper contains the results of a study of the spectral characteristics of electroluminophors of the type ZnS-Cu, Mn in an alternating field. The spectral characteristics were measured with the help of a UM-2 monochromator and a FEU-32 photomultiplier with a known spectral characteristic. The brightness was measured by a selenium photocell whose spectral sensitivity curve was matched to the visibility curve of the human eye with the help of suitable filters. The measurements were made on solid electroluminescent condensers with a thickness of the order of 70 to 100 μ.

Figure 1 shows the relative change in spectral composition of radiation from the double-activator (two-color) electroluminophor ZnS-Cu, Mn as a function of the voltage for the frequency f = 600 cps. As is evident from this figure, the radiation of this electroluminophor contains two main bands with peaks at 520 and 580 mμ. Changes in the voltage cause a re-distribution of the intensity in these bands. At 400 volts, the green radiation band with a maximum at 520 mμ predominates. Increasing the voltage to 1100 volts leads to a preponderance in the spectrum of the yellow band with a maximum at 580 mμ. Visually, the color of luminescence of the electroluminescent capacitor changes from green to yellow as the voltage is increased.

At low frequencies, of the order of 50 cps, the luminescence is dominated by the yellow band, no matter what the value of applied voltage (Fig. 2). The intensity of this band was assigned the value of 100%. The intensity of the green band was so small that for practical purposes the radiation was assumed to be yellow even at low voltages; when the voltage was increased, the yellow band, just as in the preceding case, increased more rapidly than did the green band. As the frequency was increased, the relative intensity of the yellow band became smaller for a given field gradient (Fig. 3). As the voltage increased, however, the yellow band again grew more rapidly in intensity than the green one. The intensity of the green band was taken to be 100% in Fig. 3. The change of the luminescent color from green to yellow occurred under the action of very high gradients which, for layers of the form used in these experiments, led to a breakdown of the capacitor.

Figure 4 shows how the brightness of the yellow (1) and green (2) components of the luminescence from a two-color electroluminophor ZnS-Cu, Mn depends on voltage; logarithmic scales are used.

The brightness measured at the maximum of the two

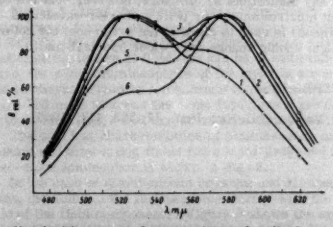


Fig. 1. The spectral composition of radiation from the two-center electroluminophor ZnS-Cu, Mn as a function of voltage at a frequency of 600 cps. Voltage (in volts): Curve 1—400; curve 2—600; curve 3—800; curve 4—900; curve 5—1000; curve 6—1100.

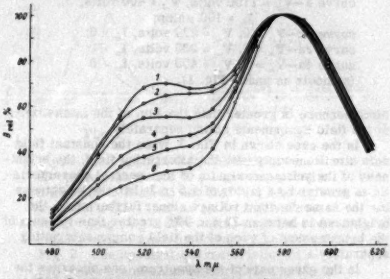


Fig. 2. Spectral characteristics of the two-center electroluminophor ZnS-Cu, Mn at a frequency of 60 cps. Voltage (in volts): Curve 1—500; curve 2—700; curve 3—800; curve 4—900; curve 5—1000; curve 6—1100.

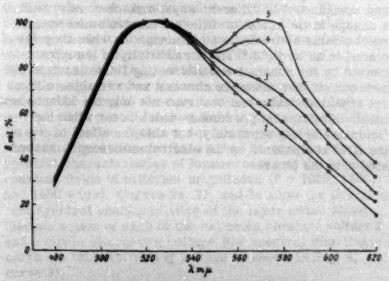


Fig. 3. Spectral characteristics of the two-center electroluminophor ZnS-Cu, Mn at a frequency of 2000 cps. Voltage (in volts): Curve 1—300; curve 2—500; curve 3—700; curve 4—900; curve 5—1000

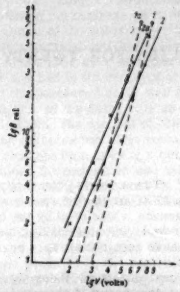


Fig. 4. Brightness of luminescence of the yellow (1, 1a) and green (2, 2a) components of single center and double center electroluminophors as a function of voltage. Curves 1, 2—the double-center electroluminophor ZnS-Cu, Mn; curve 1a—single center ZnS-Cu; curve 2a—single center ZnS-Cu, Mn.

bands with the help of two suitable narrow-band filters (SZS-18 and ZS-7 for the green band and ZS-7 and OS-13 for the yellow band) was taken to be a measure of brightness of the green and yellow components.

The brightness of both the yellow and the green radiation depends on the voltage according to a power law, namely, $B \approx V^{\alpha}$. The exponent α is larger for the yellow component than for the green ($\alpha_y = 4$; $\alpha_g = 2.4$). For small voltages, the brightness of the green component was greater than that of the yellow component; then, at a certain gradient the brightnesses became equal and, finally, at large voltages the brightness of the yellow components exceeded the brightness of the green, which of course led to a change in the observed color of the luminescence.

On the basis of the data presented here, it is possible to state that the intensity of the radiation band associated with the manganese activator increases more rapidly with voltage than the intensity of the green band due to the copper activator. These data were obtained on electroluminophors in which every crystallite contained both manganese and copper luminescent centers. It was of interest to compare these data with the characteristic radiation of yellow-manganese electroluminophors which contain practically no green band, and of green electroluminophors of the type ZnS-Cu.

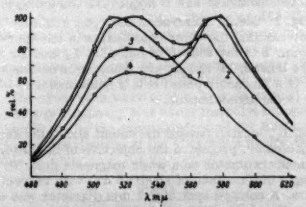


Fig. 5. Spectral characteristics of "mixed" electroluminophors at a frequency of 200 cps. Voltage (in volts): Curve 1—400; curve 2—1000; curve 3—1200; curve 4—1300.

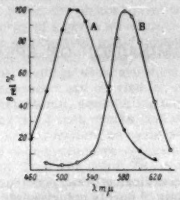


Fig. 6. Spectral characteristics of single-color green ZnS-Cu(A) and yellow ZnS-Cu, Mn(B) electroluminophors at a frequency of 200 cps.

Figure 4 shows the brightness curves for single color electroluminophors; curve 1a is for a yellow ZnS-Cu luminophor and curve 2a is for the green ZnS-Cu, Mn luminophor. The shapes of curves 1a and 2a are identical with those of curves 1 and 2.

The exponents $\alpha_{y_a} = 3.9$ and $\alpha_{g_a} = 2.4$ coincide almost exactly with α_y and α_g.

Investigation of the brightness characteristics of a series of similar luminophors showed that, in all cases, the steepness of the B(V) characteristic of the yellow manganese luminophor increases more rapidly with increasing voltage than that of the green luminophor.

Finally, the spectral and brightness characteristics of mixtures of green ZnS-Cu and yellow ZnS-Cu, Mn were obtained. The mixtures were obtained by simple mechanical mixing of the powders, and the capacitor was prepared as usual by pulverizing a suspension of the luminophor in a dielectric medium. Spectral characteristics at a frequency of 200 cps are shown in Fig. 5. The radiation spectrum of each of the luminophors which entered the mixture is shown in Fig. 6.

Just as in the case of an electroluminophor containing yellow and green luminescent centers in a single crystal, the yellow band of the mixture increased more rapidly with field than the green band, and the color of the mixed luminophor changed.

From the data presented above it is possible to conclude the following: (1) The intensities of the yellow radiation band which is characteristic of manganese, and the green band of radiation of copper change with voltage, each according to its own law; these laws are independent of whether the acts of radiation by both centers occur in the same crystal, or whether the manganese and copper centers are located in different crystals; (2) The intensity of the yellow radiation band increases more rapidly with voltage than the intensity of the green band; (3) It can be assumed that the fact that the intensity of the band from one of the centers does not depend on the presence of the other center shows that the radiation mechanisms of the green (copper) and yellow (manganese) centers differ from each other.

DETERMINATION OF SPECTRUM COLOR COORDINATES FOR TWENTY-SEVEN NORMAL OBSERVERS

N. I. Speranskaya

Received 8 April 1959

The color coordinates of the spectrum were determined on the basis of purely colorimetric correlations with energy measurements for twenty-seven normal observers with a visual field of 10 deg.

It was shown that the results obtained as a whole agreed satisfactorily with the measurements of Stiles for a group of 50 observers, in spite of considerable difference in experimental conditions.

The data obtained, together with those of Stiles, were arranged basically in a table of values of the color coordinates of a spectrum with uniform energy distribution, presented for acceptance at the sessions of the International Illumination Commission (Brussels, 1959).

1. At present, all colorimetric computations and measurements are based on the color sensitivities of the average eye, expressed in the form of three-color coordinates of colors of the uniform-energy spectrum by the International Commission on Illumination (MOK) in 1931.[1] These data were determined on the basis of the experimental results of Guild[2] and Wright,[3] obtained by them in the form of coordinates of color intensity from determination of the value of visual intensity for the standard observer, in 1924. Thus, the coordinates of spectral color $\bar{r}$, $\bar{g}$, and $\bar{b}$, were determined from the relations

$$r_\lambda = \frac{r_\lambda v_\lambda}{L_T}; \quad g_\lambda = \frac{g_\lambda v_\lambda}{L_T}; \quad b_\lambda = \frac{b_\lambda v_\lambda}{L_T},$$

in which r_λ, g_λ, and b_λ are color coordinates, v_λ are values of visibility, and L_T is the intensity of a single color, determined by the intensity of the basic colors; that is, $L_T = rL_R + gL_G + bL_B$. These data were obtained from a group of observers of 17 persons, with a visual field of 2 deg.

Later, however, Jacobsen[4] and Judd[5] reported some discrepancy between visual evaluations of color of two samples of titanium white and the results of determinations of their color on the basis of data of the standard observer of 1931. The authors came to the conclusion that the data for the standard observer were too low in the region $\lambda < 430$ mμ.

In more recent times, the trend has been to use larger visual fields in colorimetry.[6]

Little by little the idea has gained acceptance that the method of determining the coordinates of spectral colors, derived from the coordinates of color intensity and the visibility curve, is in principle inadequate, since in that process the comparison of heterochromic intensities is involved.

All of these considerations impelled the 12th session of MOK, in 1951, to recommend carrying out new determinations of the color coordinates of the spectrum on the basis of purely colorimetric correlations using energy measurements and a visual field of 10 deg.

Accordingly, such work was begun in the National Physical Laboratory in England by Stiles,[8] and, somewhat later, by us.[9] Stiles obtained preliminary date for 2 deg and 10 deg visual fields for a group of observers of 10 persons, and reported the work at the 13th session of MOK in 1955.[10] (Translator's note: I have chosen to use the designation MOK for the International Commission on Illumination because it was used by the author. It stands for Mezhdunarodnoi Osvetitel'noi Komissii. The designation ICI might have been chosen as a reasonable alternative, of course).

Later, measurements at 10 deg visual field were extended by him on a group of observers of 50 persons.[11] Our apparatus[9] was finally somewhat improved, and was used to obtain measurements for a group of 27 observers with a visual field of 10 deg, with a central zone of about 2 deg screened out in order to avoid the so-called "Maxwell's spot."

2. Figure 1 shows the arrangement of the basic parts of the apparatus. The filament of a lamp S (500 watts, 110 volts, type PZh-7) was projected by means of a lens L_1 on the slit of a monochromator M_1. Monochromatization was accomplished by two monochromators, M_1 and M_2, arranged with their dispersions subtracting.

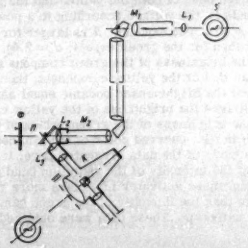


Fig. 1. Sketch illustrating the apparatus for determining the color coordinates of the spectrum. S is the source of light; L_1, L_2, and L_3 are lenses; M_1 and M_2 are monochromators; П is a magnesia plate; K is a colorimeter; Φ is the photoelement.

The lens L_2, located beyond the output slit of the second monochromator, projected the objective of the latter tube of the monochromator on a white magnesia plate П, set at an angle of incidence of about 45 deg with respect to the beam. A colored spot of 5-7 mm diameter was obtained on the plate. The color of the spot was measured by the colorimeter K of the system of GOI (the State Optical Institute)[12] arranged approximately normal to the white plate. The auxiliary lens, together with lenses of the colorimeter, projected the colored spot onto the pupil of the colorimeter which cut out the central part.

The component colors of the colorimeter were determined by red, green, and blue light filters with color tones of about 640, 545, and 465 mμ.

The proportions of the intensities transmitted through these light filters, read on the scale of the color-

imeter, were calibrated using a photoelement, whereupon the corresponding corrections were determined.

The field of vision of the colorimeter had an angular size of 10 deg with a vertical line and a black background. The central part of the field over an angle of about 2 deg was screened out and had in its center a bright fixation point. Dilution of the measured color was accomplished by purple light filters, of the same type as the color filters of the colorimeter. The amount of dilution of the color filters of the colorimeter. The amount of dilution of the color was changed by means of a central wedge which was introduced far enough so that the dilution could be measured by two primary colors. Measurements were carried out at 10 mμ intervals, from 400 to 720 mμ.

The energy of the monochromatic radiations were measured by means of photoelements Φ, set in place of the white magnesia plate Π. In the region from 400 to 640 mμ, measurements were made by use of a selenium photoelement; from 640 to 720 mμ, because of the fatigue of the selenium photoelement in this range, a silver sulfide element was used. The silver sulfide photoelement was placed in a thermostat (temperature = 29°C).

Relative curves of the spectral sensitivity of the photoelements were obtained by means of thermoelements. Proportionality of the photocurrents on illumination were checked, and it was found that departure from linearity did not exceed 1.5-2%.

Values of the half-widths of the spectral regions used in the measurements are shown in Table 1 (second line). The voltage on the lamp of the monochromator had to be changed in the measurements within the limits from 70 to 150 volts. The voltage on the lamp of the monochromator and on the lamp of the colorimeter was stabilized. The intensity of the visual field was determined by means of an auxiliary experiment. Corresponding values of the illumination on the retina in Trolands are shown in Table 1 (third line).

Table 1

λ (mμ)		400	450	500	550	600	650	700	720
Half-width (mμ)		6	2.8	2.7	2.4	3.2	4.3	6.7	7.4
Illumination (Trolands)	etc.	1—2	4	20	35	40	20	4	3

The selectivity of reflection of the white magnesia plate was tested, whereupon it was demonstrated that the departure from a neutral tint in the region 400-420 mμ did not exceed 3%. At the limits of the spectrum in front of the entrance slit red or blue light filters for removing scattered light were set. In the measurements, 27 observers participated, of whom 23 were women and 4 were men. The observers were proven to have normal color vision in a preliminary test using the polychromatic table of Rabkin[13] and on the anomaloscope of the Rautian system.[14] The distribution of the observers by age is shown in Table 2.

Table 2

Age of the observers	Number of observers
From 18 to 23	14
From 25 to 27	4
From 30 to 37	5
47	3
56	1

Eleven of the observers experienced colorimetric measurements. The rest were trained for two or three days before starting on the measurements.

3. The measurements were carried out in the following manner: First, the photoelement was used to measure the energy of a given wavelength of monochromatic light; then an observer would measure the color three times, after which the energy measurement would be repeated. The readings were averaged. Measurements in this sequence were carried out over the whole spectrum for each 10 mμ, constituting one cycle. Each observer carried out 3 such cycles, and some of them, 2 more supplementary cycles; no cycle was incomplete.

The data of each cycle were reduced to an equal-energy standard. Thus, the color $\overline{T}_{S\lambda}$ of the monochromatic radiation of unit power is determined by the coordinates $\frac{a}{\frac{m}{v}}, \frac{b}{\frac{m}{v}}, \frac{c}{\frac{m}{v}}$

$$\overline{T}_\lambda = \left(\frac{a}{\frac{m}{v}}\right)_\lambda R_0 + \left(\frac{b}{\frac{m}{v}}\right)_\lambda G_0 + \left(\frac{c}{\frac{m}{v}}\right)_\lambda B_0,$$

where R_0, G_0, and B_0 are the primary colors of the apparatus, a, b, and c are readings on the scale of the colorimeter, m is the reading of the galvanometer, and v is the relative sensitivity of the photoelement.

The results obtained by each observer in the system R_0, G_0, and B_0 from 3 or 5 cycles were averaged. After a period during which the measurements of the 27 observers were being made, the primary colors of the apparatus were changed, so that it would not be proper to calculate the mean of all 27 observers in one system of primary colors. Therefore the mean value of each observer was recalculated in one and the same system of colors of monochromatic radiation: 645.2, 526.3, and 444.4 mμ*, and only after this was the average calculated.

*This system of primary colors was chosen by Stiles for representing his experimental data.

4. The mean values of the coordinates $\overline{r}_\lambda$, $\overline{g}_\lambda$, and $\overline{b}_\lambda$ of the colors of an equal-energy spectrum for 27 observers in the system 645.2, 526.3, and 444.4 mμ are presented in Table 3 and Fig. 2.

Table 3

λ	$\overline{r}_\lambda \pm s\overline{r}_\lambda$	$\overline{g}_\lambda \pm s\overline{g}_\lambda$	$\overline{b}_\lambda \pm s\overline{b}_\lambda$
400	0.33 ± 0.05	−0.11 ± 0.03	0.96 ± 0.25
5	0.28 ± 0.12	−0.13 ± 0.04	1.57 ± 0.48
10	0.45 ± 0.13	−0.16 ± 0.04	2.65 ± 0.53
20	0.71 ± 0.19	−0.31 ± 0.08	5.22 ± 0.87
30	0.62 ± 0.15	−0.31 ± 0.09	7.66 ± 0.51
40	0.28 ± 0.09	−0.16 ± 0.05	9.70 ± 0.27
50	−0.46 ± 0.15	0.27 ± 0.06	9.98 ± 0.27
60	−1.28 ± 0.30	0.90 ± 0.14	9.09 ± 0.55
70	−2.62 ± 0.41	1.94 ± 0.24	7.09 ± 0.57
80	−3.60 ± 0.48	3.09 ± 0.29	4.46 ± 0.35
90	−4.14 ± 0.68	4.20 ± 0.34	2.16 ± 0.24
500	−4.42 ± 0.51	5.97 ± 0.36	1.10 ± 0.13
10	−3.85 ± 0.53	7.70 ± 0.33	0.497 ± 0.095
20	−1.98 ± 0.45	9.30 ± 0.45	0.212 ± 0.073
30	1.70 ± 0.44	10.3 ± 0.3	−0.070 ± 0.059
40	5.20 ± 0.66	10.7 ± 0.2	−0.303 ± 0.066
50	10.3 ± 0.8	10.3 ± 0.2	−0.47 ± 0.12
60	16.1 ± 1.0	9.36 ± 0.25	−0.46 ± 0.12
70	21.6 ± 1.2	7.58 ± 0.25	−0.42 ± 0.13
80	26.0 ± 1.4	5.72 ± 0.22	−0.36 ± 0.11
90	29.0 ± 1.3	3.85 ± 0.15	−0.32 ± 0.10
600	30.5 ± 1.3	2.34 ± 0.12	−0.297 ± 0.08
10	28.7 ± 1.3	1.23 ± 0.09	−0.232 ± 0.060
20	24.8 ± 1.2	0.52 ± 0.03	−0.167 ± 0.042
30	18.9 ± 0.9	0.167 ± 0.019	−0.104 ± 0.028
40	12.5 ± 0.29	0.022 ± 0.037	−0.0123 ± 0.0006
50	8.02 ± 0.21	−0.021 ± 0.036	0.0117 ± 0.005
60	4.58 ± 0.19	−0.018 ± 0.005	0.0111 ± 0.005
70	2.46 ± 0.11	−0.014 ± 0.003	0.0172 ± 0.0010
80	1.26 ± 0.07	−0.0168 ± 0.0012	0.0050 ± 0.002
90	0.612 ± 0.031	−0.0040 ± 0.0009	0.0027 ± 0.001
700	0.300 ± 0.018	−0.0022 ± 0.0008	0.0016 ± 0.001
10	0.140 ± 0.008	−0.0012 ± 0.0004	0.0014 ± 0.0009
20	0.061 ± 0.004	−0.0006 ± 0.0004	0.0007 ± 0.0005

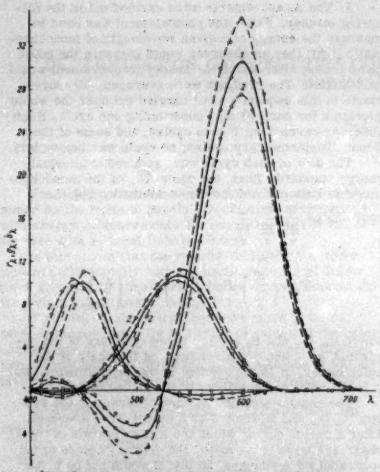


Fig. 2. Mean values of the color coordinates of an equal-energy spectrum for 27 observers. Curve 1—mean values; curve 2—limits of variation.

The limits within which the values of color coordinates of the 27 observers vary are shown in the figure by dotted lines. It is proper to evaluate these differences only at the largest, i.e., the most nearly correct value of the coordinate. Furthermore, it is shown that the observers differed most of all in the limit of the blue end of the spectrum. This may be due to the pigmentation of the retina and the eye media. For the wavelength 405 mμ of the "blue" the coordinates vary by a factor of 14; at the wavelength 410 mμ, they vary up to 6, and for λ = 420 mμ, only by a factor 2. In the red and green part of the spectrum the readings of the observers differ only by the factor 1.2.

5. We computed from the data of 7 observers (Table 4) the mean relative error

$$\frac{\Delta a}{a}, \frac{\Delta b}{b}, \frac{\Delta c}{c}$$

in the system of primary colors chosen, for several wavelengths. Comparison of the values of Δa/a, Δb/b, and Δc/c for different wavelengths shows that the errors are large to the degree that the measured quantities are small. Conversely, the smallest relative errors are found for the largest values of the "red," "green," and "blue" coordinates. For the "blue" coordinate in the region 440-460 mμ the smallest error amounts to 5%, for example; for the "green"(530-550 mμ) and for the "red" (590-610 mμ), it is about 3%. Different measurements in the blue part of the spectrum, even those of the experienced observers, were occasionally accompanied by large errors.

Table 4

λ	420	430	440	450	460	470	530	540	550	590	600	610
Δa/a	7.8	8.3	8.4	11.6	61.8	10.2	5.5	11.5	12.5	3.9	3.2	3.0
Δb/b	8.4	7.7	7.8	9.2	13.8	10.7	2.5	2.8	1.9	3.9	3.0	4.1
Δc/c	7.2	7.1	5.5	4.8	5.3	5.4	60.8	26.5	18.8	18.0	12.9	17.3

6. If one compares the difference between the curves of the observers and their errors, it turns out that the errors in the data of a given observer are less than the maximum differences between observers. In Table 3, along with the mean values of the color coordinates of the spectrum, is shown also the mean variation $\Delta\bar{r}_\lambda$, $\Delta\bar{g}_\lambda$, and $\Delta\bar{b}_\lambda$ which characterizes differences in the color vision of the observers. These variations indicate to what degree, in practice, the value of the color coordinates of the spectrum is a characteristic of the standard observer.

7. In Fig. 3 our data are compared with those of Stiles for 50 observers. In this, the units of the primary colors, 645.2, 526.3, and 444.4 mμ (the same for our data and those of Stiles) were reduced to the same scale. The largest differences are observed in the yellow-orange part of the spectrum for the "blue" coordinates; here the differences reach five times and even ten times the magnitude itself. In the region 450-500 and 400-420 mμ differences are observed for all three coordinates. The "green" curve of Stiles in its absolute value, is somewhat larger in comparison with our curve on both sides of the maximum in a somewhat symmetrical manner. There is some difference also at the peaks of the maxima of the "red" curves.

The explanation of the origin of these differences is of interest. Generally speaking, they may be ascribed to the following causes: (1) peculiarities in the color vision of the two groups; (2) differences in the experimental conditions, and finally, (3) possible differences in the systematic errors.

For clarification of the character of these differences we used the results of measurements of the ob-

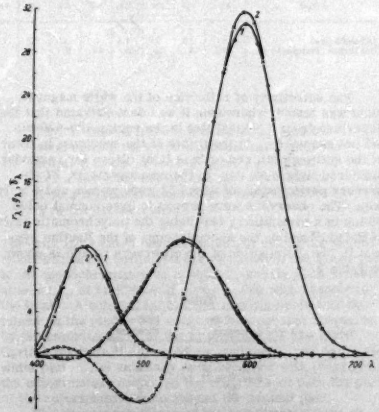


Fig. 3. Results of measurement of the color coordinates of the spectrum on different equipment. Curve 1—averaged data of the author; curve 2—averaged data of Stiles.

server E. N. Iu., obtained on the apparatus of Stiles at the time of the Symposium on Visual Problems of Color in September 1957, and on our apparatus. This and other data of E. N. Iu. are shown in Fig. 4. Comparison of the curves in Fig. 4 shows that, as a whole, observer E. N. Iu. gave somewhat different results on the two set-ups, but consistent in character with the differences between the averaged values (See Fig. 3). Consequently, the departures between the data of our equipment and that of Stiles can be traced not so much to the peculiarities of the color vision of the two groups of observers, but most likely to different experimental conditions. Of most importance as a difference between our apparatus and that of Stiles, would be the intensity of the field of vision, which was 30 to 40 times as great with Stiles' as with ours. We have attempted to explain how the difference in intensity would affect the "blue" coordinate in the yellow part of the spectrum since especially large differences are observed for that coordinate. Unfortunately, we were not able to achieve the same level of intensity as Stiles used; therefore we tried lowering the intensity instead, and made some supplementary measurements for a wavelength of 570 mμ for two intensities. In this, the ratio of the coordinates in the system R_0, G_0, and B_0 for large and small intensities were: in the "red" coordinate, 3.6; in the "green," 3.8; and in the "blue," 2.9. Thus, with decrease in intensity the "blue" coordinate was perceptibly larger in comparison with the other two.

The same increase in the "blue" coordinate (in its negative part) with decrease in intensity is shown in the work of Stiles.[15] He showed that for intensities below 100 Trolands (field of vision of 10 deg) considerable increase in the "blue" coordinate was observed. For the "green" coordinate the author observed some influence of intensity also. The "red" coordinate was not perceptibly affected by intensity. Additional measurements of ours in the blue part of the spectrum at levels of intensity 4.3 and

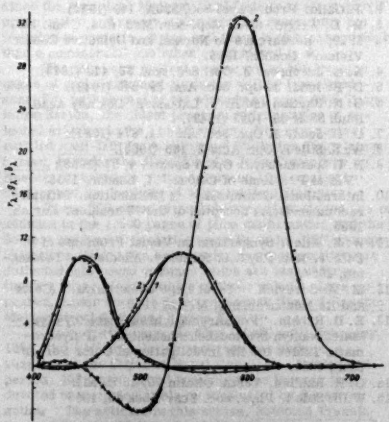


Fig. 4. Results of the measurement of color coordinates of the spectrum by observer E. N. Iu. on different set-ups.
1—on the apparatus of GOI (State Optical Institute);
2—on the apparatus of Stiles.

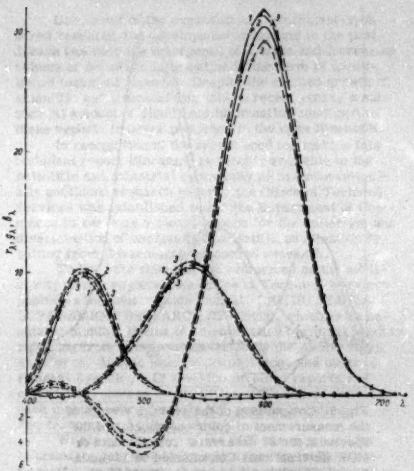


Fig. 5. Comparison of results of measurement of the color coordinates of the spectrum by GOI and Stiles, with the magnitude of the mean variation. Curve 1—data of Stiles; curve 2—data of the author; curve 3—limits of mean variation.

1.5 Trolands, and for wavelengths 440, 450, and 460 mμ, for 7 observers showed changes in all three coordinates.

We converted the results of measurement of one observer (V.S.L.) at the wavelength 460 mμ from the system R_0, G_0, B_0 into the system 645.2, 526.3, and 444.4 mμ. The results of the conversion, corresponding to three levels of intensity, are given by the three equations:

4 Trolands $\overline{Ts}_{460} = -1.04R + 0.94G + 0.83B$
3 Trolands $\overline{Ts}_{460} = -0.92R + 0.90G + 0.93B$
1.5 Trolands $\overline{Ts}_{460} = -0.89R + 0.86G + 1.03B$

Comparing the differences in Figs. 3 and 4, with intensity change, of the coordinates in these equations, for $\lambda = 460$ mμ, it is readily concluded that differences in the "blue" and "green" coordinates may be completely explained by a difference in the intensity level of our observations as compared to those of stiles. Some discrepancy in the "red" coordinate was obtained by observer E. N. Iu. (Fig. 4). It is possible that here there may be errors in the measurement. Differences in the mean values (Fig. 3) corresponding to the discrepancy were not observed.

Thus one can conclude that the differences between our data and those of Stiles are due basically to differences in the level of intensity of the visual field. If we compare these differences with the mean variation in color vision of our group—Δr, Δg, Δb—as is done in Fig. 5, one can see that beyond the limit of the mean variation, a difference in the "blue" coordinate emerges, mainly in the negative part. Positive values of the "blue" coordinate at certain points are also different by more than the mean variation. As far as the "green" and "red" coordinates are concerned, the differences for them lie

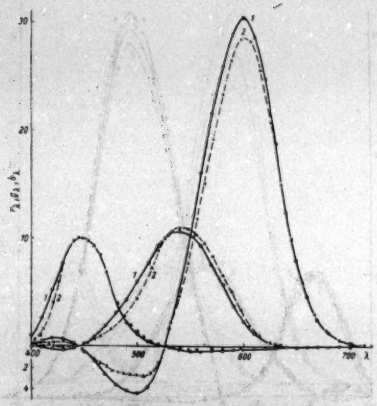


Fig. 6. Comparison of the average results of the measurement of color coordinates of the spectrum for 27 observers from the data of MOK (International Commission on Illumination) 1931. Curve 1—mean values of 27 observers (10 deg field); curve 2—values of MOK (2 deg field).

within the limits of mean variation. Thus, our data and the data of Stiles, except for the negative values of the "blue" coordinate, are in satisfactory agreement in spite of the differences in the experimental conditions, mainly in the level of intensity.

8. It is interesting to compare the mean values for 27 observers with the data of MOK (International Commission on Illumination) of 1931. They are shown together in Fig. 6, expressed in the system of primary colors 645.2, 526.3, and 444.4 mμ. One can notice differences in all three coordinates. Comparison of these differences with differences between our mean values and the values of Stiles (Fig. 3) for a visual field of 10 deg leads to the conclusion that the size of the visual field has no larger an effect on the results than any other experimental condition.

Figure 7 shows the lines of spectral color intensity in the r, g plane, according to the data of MOK, of Stiles, and of the author. The scales of the primary colors were chosen so that the coordinates of color intensity for an equal-energy source E would be equal, i.e., $\frac{1}{3}$, $\frac{1}{3}$, and $\frac{1}{3}$. Here also it is evident that the difference in the coordinates of color intensity r and g, for 2 and 10 deg visual field are greater than the difference between our data and the data of Stiles, obtained at 10 deg, but under different conditions of experimentation.

9. The chairman of the committee of MOK on colorimetry, Judd, carried out an analysis of the data of

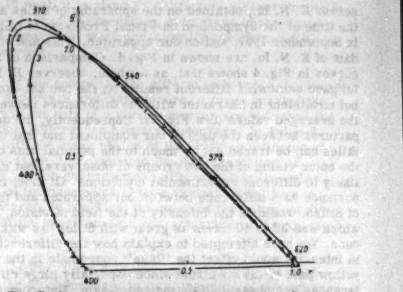


Fig. 7. Lines of spectral coloration according to different data. Curve 1—data of Stiles; curve 2—data of the author; curve 3—data of MOK. (International Illumination Commission)

Stiles and ours, compiling a detailed table of the values of the color coordinates of an equal-energy spectrum, which will be presented for the consideration of the meeting of the MOK in Brussels in the summer of 1959. (This was received in February 1959 by the Standing Commission on Colorimetry of the All-Union Research Institute of Metrology).

REFERENCES

1. T. Smith and J. Guild. Trans. Opt. Soc. **33**, 77 (1931-2).
2. J. Guild. Proc. Phys. Soc. **230A**, 149 (1932).
3. W. D. Wright. Spec. Rep. Ser. Med. Res. Coun. 139, 1929; "Researches on Normal and Defective Colour Vision." London, 1946.
4. A. E. Jacobsen. J. Opt. Soc. Am. **38**, 442 (1948).
5. D. B. Judd. J. Opt. Soc. Am. **39**, 945 (1949).
6. G. N. Rautian and H. V. Labonova. Doklady Acad. Nauk SSSR **68**, 1025 (1949).
7. D. B. Judd. J. Opt. Soc. Am. **41**, 874 (1951).
8. W. S. Stiles. Opt. Acta **2**, 166 (1955).
9. N. I. Speranskaya. Opt. i Spektr. **4**, 87 (1955); "Visual Problems of Colour," I, London, 1958.
10. International Commission on Illumination. Official recommendation accepted of the 13 session. Zurich, 1955.
11. W. S. Stiles. Symposium on Visual Problems of Colour. Nat. Phys. Laboratory. Middlesex, Teddington, 1957.
12. M. M. Gurevich. "Tsvet i ego izmereniya." (Color and its Measurement), M.-L., 1950.
13. E. B. Rabkin. "Polikhromaticheskie tablitsy dlya issledovaniya tsvetooshchushcheniya." (Polychromatic Tables for the Investigation of Color Perception), 1954.
14. G. N. Rautian. Vestn. Oftalm 10, 18 (1954).
15. W. S. Stiles. Phys. Soc. Year Book **44**, 1955

THE AMERICAN MATHEMATICAL SOCIETY PROGRAM OF RUSSIAN TRANSLATION

A greatly increased program of translation of Russian mathematics is under way at the American Mathematical Society, under the sponsorship of the National Science Foundation. Two new projects are being planned, one to bring the results of Russian research in mathematics to American mathematicians more rapidly, and the other to make available Russian books which would not otherwise be published in English. In addition, the currently existing program of selected Russian translations is being expanded to cover probability and statistics as well as pure mathematics.

The first of these projects is a new subscription journal, Soviet Mathematics -- Doklady, which will contain translations of the entire pure mathematics section of the Doklady Akademii Nauk SSSR, the Reports of the Academy of Sciences of the USSR. The Doklady, which consists of short reports of current research in the USSR, will provide a comprehensive, up-to-date survey of what is going on in Soviet mathematics. The AMS journal will appear six times a year, each issue corresponding to one volume of the Russian Doklady, which is issued three times a month, six issues constituting a volume.

The second new project is the translation and publication by the American Mathematical Society of Russian books. Three books have been tentatively scheduled for 1960, and several others are under consideration. The three to be undertaken in 1960 are: Some Applications of Functional Analysis in Mathematical Physics, by S. L. Sobolov, 225 pages; Some Questions in the Theory of Moments, by N. Akhiezer and M. Krein, 255 pages; and Theory of Analytic Functions of Several Complex Variables, by B. A. Fuks, 475 pages.

The Society expects to make available books which, although they are valuable contributions to mathematical research, are too specialized to sell widely and are therefore not attractive to commercial publishers. Also, since the American Mathematical Society is a non-profit organization and receives Government support for the translation projects, it can sell these books more cheaply than a commercial publisher could afford to do.

The third new project, under which 500 Russian pages of probability and statistics will be translated annually, will be part of the already existing AMS Translation Series, the oldest program of translation of selected articles in the United States. The new series, entitled AMS-IMS Probability and Statistics Translation Series, is under the direction of a Joint Committee on Russian Translation of the American Mathematical Society and the Institute of Mathematical Statistics.

These 500 pages of probability and statistics are in addition to the 1,500 pages of pure mathematics that the Society has been translating annually under NSF sponsorship since 1954. The articles in pure mathematics are collected into bound volumes which are issued three times a year. So far twelve of these volumes have appeared, under the title Selected Translations of Russian Mathematical Articles, Series II.

From its beginning in May, 1948, until February, 1954, the AMS translation program was under the auspices of the Office of Naval Research. During that period, 105 paper-bound booklets were issued, each devoted to a single article or to several by the same author. The articles in this series, Selected Translations of Russian Mathematical Articles, are now out of print.

TECHNICAL INFORMATION DIVISION OF THE OFFICE OF TECHNICAL SERVICES

One result of the expansion of Government-sponsored research and development programs in the past decade has been the emergence of a large and increasing volume of scientific information in the form of unpublished technical reports. Despite the marked growth of scientific and technical journals in recent years, a substantial amount of significant information contained in these reports is never published in the open literature.

In recognition of the urgent need for making this technical report literature as readily available to the scientific and industrial community as are conventionally published research papers, the Office of Technical Services was established within the Department of Commerce to serve as a clearinghouse for the collection and dissemination of unclassified scientific information resulting from Government-sponsored research.

To keep the scientist fully informed on the availability of new reports, the Office of Technical Services publishes the subscription journal, UNITED STATES GOVERNMENT RESEARCH REPORTS, which is an annotated monthly listing of scientific and technical reports resulting from research conducted by the Army, Navy, Air Force, Atomic Energy Commission, and other Federal Agencies. Of the 1100 or more reports received and released by the Office of Technical Services each month, approximately 10% pertain to optics, spectroscopy and allied subjects.

Within the past year, the OTS has expanded its information services to include a foreign technical information program which has as its objective the collection and dissemination of translations of scientific and technical material in Russian and other languages. The availability of this information is announced in the semi-monthly journal, TECHNICAL TRANSLATIONS, which is published in cooperation with the Special Libraries Association Translation Center, John Crerar Library, Chicago, and all translations which can be obtained from the OTS, SLA, cooperating foreign governments, and commercial translating agencies are listed. The OTS is currently announcing about 1000 technical translations every month; of these almost 15% deal with optics and related fields.

The OTS also publishes and disseminates complete translations of abstracts from the Soviet abstract journal series, the Referativnyy Zhurnal. The largest section of the physics series is optics which lists as its subdivisions geometrical optics, optical media, optical techniques, physical optics, luminescence, spectroscopy, optical methods of analysis, instrumentation, X-rays, physiological optics, photometry, colorimetry, and photography.

The OTS also provides a comprehensive bibliographic and reference service with respect to U.S. Government research reports and technical translations. In this connection, the Technical Information Division of the OTS is prepared to locate specific reports and translations, not only by identified title and author, but also on general and specific subjects within the fields of science, and technology. It also furnishes bibliographical assistance where a comprehensive subject search is required. Formal selective bibliographies on optics, spectroscopy and related subjects are available, and in addition, several hundred title lists in fields of science and technology have been prepared as a result of literature searches.

SOVIET PHYSICS JOURNALS PUBLISHED IN ENGLISH BY THE AMERICAN INSTITUTE OF PHYSICS

Soviet Physics - JETP

A translation, beginning with 1955 issues of "Journal of Experimental and Theoretical Physics" of the USSR Academy of Sciences. Leading physics journal of Soviet Union. Similar to "The Physical Review" in quality and range of topics. Outstanding new work is most likely to appear in this journal.

Soviet Physics - SOLID STATE

A translation, beginning with 1959 issues of "Fizika Tverdogo Tela" of the USSR Academy of Sciences. Offering results of theoretical and experimental investigations in the physics of semiconductors, dielectrics, and on applied physics associated with these problems. Also publishes papers on electronic processes taking place in the interior and on the surface of solids.

Soviet Physics - TECHNICAL PHYSICS

A translation, beginning with the 1956 issues of the "Journal of Technical Physics" of the USSR Academy of Sciences. Contains work on plasma physics and magnetohydrodynamics, aerodynamics, ion and electron optics and radio physics. Also publishes articles in mathematical physics, the physics of accelerators and molecular physics.

Soviet Physics - ACOUSTICS

A translation, beginning with 1955 issues of "Journal of Acoustics" of USSR Academy of Sciences. Devoted principally to physical acoustics but includes electro, bio, and psycho acoustics. Mathematical and experimental work with emphasis on pure research.

Soviet Physics - DOKLADY

A translation, beginning with 1956 issues of "Physics Sections" of Proceedings of USSR Academy of Sciences. All-science journal offering four-page reports of recent research in physics and borderline subjects.

Soviet Physics - CRYSTALLOGRAPHY

A translation, beginning with 1957 issues of the journal "Crystallography" of USSR Academy of Sciences. Experimental and theoretical papers on crystal structure, lattice theory, diffraction studies, and other topics of interest to crystallographers, mineralogists, and metallurgists.

SOVIET ASTRONOMY - AJ

A translation, beginning with 1957 issues of "Astronomical Journal" of USSR Academy of Sciences. Covers various problems of interest to astronomers and astrophysicists, including solar activity, stellar studies, spectroscopic investigations of radio astronomy.

Soviet Physics - USPEKHI

A translation, beginning with September, 1958 issues of "Uspekhi Fizicheskikh Nauk" of USSR Academy of Sciences. Offers reviews of recent developments comparable in scope and treatment to those carried in "Reviews of Modern Physics." Also contains reports on scientific meetings within the Soviet Union, book reviews, and personalia.

AMERICAN INSTITUTE OF BIOLOGICAL SCIENCES TRANSLATION PROGRAM

The American Institute of Biological Sciences is currently translating and publishing seven Russian research journals in biology. These journals are translated with support from the National Science Foundation, which is eager that such information be more widely distributed to biologists throughout the world. It is hoped that this material will aid biologists in research, prevent duplication of work, give some idea of the work being done by Soviet scientists in the field of biology, and also bring about a better international understanding among scientists.

Because of the support of the National Science Foundation, the AIBS can offer these translations at a fraction of their publication cost, with even further price reduction to AIBS members and to academic and non-profit libraries. This reduction, the AIBS feels, places the translation within the reach of all biologists.

The journals currently being translated are: Doklady: Biological Sciences Section, Doklady: Botanical Sciences Section, Doklady: Biochemistry Section, Plant Physiology, Microbiology, Soviet Soil Science, and Entomological Review.

In addition to its program of Russian Biological Journal translations, the AIBS has instituted a separate program of translation and publication of selected Russian Monographs in biology. This program is being sponsored by the National Science Foundation.

It was felt that the program of Journal translations was not sufficient to cover all of the significant work being done in all fields of biology by Russian scientists. With the aid of competent authorities, the AIBS has translated and published six Russian monographs and one monograph is in the process of being published. In addition, several prominent monographs in various biological areas are being considered by the AIBS and the National Science Foundation for translation and publication. The monographs that have been published are: Origins of Angiospermous Plants, by A. L. Takhtajan; Problems in the Classification of Antagonists of Actinomycetes, by G. F. Gauze; Marine Biology, Trudi Institute of Oceanology, Vol. XX, edited by B. N. Nikitin; Arachnoidea, by A. A. Zakhvatkin; and, Arachnida, by B. I. Pomerantzev. The manuscript for X-rays and Plants by L. P. Breslavets is in the final stages of preparation and should be published early in 1960.

EDITOR'S NOTE

Comments on the scientific content of the translated Russian articles published in OPTICS AND SPECTROSCOPY are invited. They should be addressed as a Letter to the Editor of the Journal of the Optical Society of America and forwarded to the Editor of that journal, Dr. W. R. Brode, National Bureau of Standards, Washington 25, D.C.

TRANSLITERATION OF CYRILLIC CHARACTERS

used by the Optical Society of America

А	а	a	Р	р	r
Б	б	b	С	с	s
В	в	v	Т	т	t
Г	г	g	У	у	u
Д	д	d	Ф	ф	f
Е	е	e	Х	х	kh
Ж	ж	zh	Ц	ц	ts
З	з	z	Ч	ч	ch
И	и	i	Ш	ш	sh
Й	й	i	Щ	щ	shch
К	к	k	Ъ	ъ	"
Л	л	l	Ы	ы	y
М	м	m	Ь	ь	'
Н	н	n	Э	э	e
О	о	o	Ю	ю	yu
П	п	p	Я	я	ya

VOL. VII, NO. 5 OPTICS AND SPECTROSCOPY NOVEMBER 1959

CONTENTS

Calculation of Some Parameters of Monosubstituted Benzene Molecules by the "Metal" Model Method . . . . . A. F. Terpugova 359

Calculation and Interpretation of Vibrational Spectra of Naphthenes. III. Cyclopentane and Deuterocyclopentane . . . . . L. M. Sverdlov and N. I. Prokof'eva 363

Theory of Intensities in the Infrared Spectra of the Molecules CF_4 and C_2F_6 . . . . . L. M. Sverdlov 368

Laws of the Absorption of Infrared Radiation in Thin Layers of Some Gases. I. Coefficient of Absorption in Vibration-Rotation Bands . . . . . P. I. Bresler 371

Laws of the Absorption of Infrared Radiation in Thin Layers of Some Gases. II. Absorption of Radiation in the Vibration-Rotation Bands of Some Gases . . . . . P. I. Bresler 375

The Absorption Spectrum of Liquid and Solid Oxygen under Pressure (12,600-3000 A) . . . . . V. I. Dianov-Klokov 377

The Long Wavelength Infrared Spectrum of H_2O Vapor and the Absorption Spectrum of Atmospheric Air in the Region 20—2500 μ (500-4 cm^{-1}) . . . . . N. G. Yaroslavsky and A. E. Stanevich 380

Influence of Solvent on the Intensities of Resonating Intramolecular Vibrations of Carbon Tetrachloride . . . . . M. P. Lisitsa and L. A. Ovander 383

Influence of Temperature and of the State of Aggregation on the Intensity of Vibrational Absorption Bands of Carbon Tetrabromide . . . . . M. L. Lisitsa, V. N. Malinko, and I. N. Khalinmonova 386

Spectra of Organo-Boron Compounds of the Aromatic Series . . . . . A. N. Nikitina, V. A. Vaver, N. S. Fedotov, and B. M. Mikhailov 389

Optical Investigation of the Molecular Structure of Cyanamide and Its Derivatives. II. The Infrared Spectrum and Molecular Structure of Cyanamide and Its Salts . . . . . B. I. Sukhorukov and A. I. Finkel'shtein 393

On Some Peculiarities of the Absorption Spectra of Crystals and Solutions of Thionine Violet . . . . . N. M. Melankholin and E. N. Slavnova 396

Quantum Yields of Phosphorescence and Fluorescence of Some 1-Derivatives of Naphthalene in Solutions at −196° C . . . . . V. L. Ermolaev and K. K. Svitashev 399

On the Limiting Polarization of Luminescence of Complex Molecules . . . . . G. P. Gurinovich, A. M. Sarzhevskii, and A. N. Sevchenko 401

The Effect of Elastic Deformation by Uniaxial Compression and Elongation of Crystals on the Spectra of Local Anisotropic Centers in a Cubic Lattice. I. Method . . . . . A. A. Kaplyanskii 406

The Effect of the Elastic Deformation by Uniaxial Compression and Extension of Crystals on the Spectra of Local Anisotropic Centers in a Cubic Lattice. II. Experimental Part . . . . . A. A. Kaplyanskii 409

On the Influence of Infrared Light on Luminescence of ZnS-Mn Phosphors . . . . . P. B. Jaszczyn 414

Influence of Fast Electrons on the Light Sum Stored in Cathodoluminescence . . . . . Iu. M. Popov 417

Spectral Characteristics of Electroluminescence of Some Electroluminophors in the Case of the Simultaneous Action of Constant and Alternating Fields . . . . . V. N. Favorin, G. S. Kozina, and L. K. Tikhonova 420

Voltage Dependence of the Spectral Composition of the Radiation from Certain Electroluminophors in an Alternating Field . . . . . V. N. Favorin and L. P. Poskacheyeva 422

Determination of Spectrum Color Coordinates for Twenty-Seven Normal Observers . . . . . N. I. Speranskaya 424